

IN-SITU DETECTION AND MONITORING OF
MARINE SEDIMENT POLLUTION THROUGH
ELECTRICAL CONDUCTIVITY METHODS

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TITLE ABSTRACT

MARINE SEDIMENT POLLUTION DETECTION

IN-SITU DETECTION AND MONITORING OF
MARINE SEDIMENT POLLUTION THROUGH
ELECTRICAL CONDUCTIVITY METHODS

BY

PETER WAYNE MARSHALL

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PETER WAYNE MARSHALL



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ABSTRACT

Marine sediment pollution studies are of extreme importance in analyzing water quality standards. Concentrations and identification of pollutants in the sediments when considered with flow characteristics of the water column, and pollution influent into the water column, offer indications of the ability of the water to clean itself, approach equilibrium, or deteriorate in quality.

Traditionally, sediment pollution has been identified by obtaining field samples and conducting laboratory analyses. Examining any particular area, however, involved an extensive core sampling commitment. Since many studies could not support the time and expense attendant with such a coring procedure, marine sediment sampling was disregarded.

For several years, electrical conductivity devices have been utilized to examine sediments in difficult locations. One of these devices, the microlaterolog, was used in this study to measure changing conductivity in submerged sediments caused by various pollutants. Laboratory tests were conducted on three soils: Ottawa Sand, Sodium Montmorillonite Clay, and Illite Clay, which were separately polluted with nine different materials composed of heavy metals, organics, hydrocarbons, and a pesticide. Conductivities of the sediments, interstitial waters, and the formation factors (ratio of the conductivity of water

to the conductivity of the sediment) were recorded on polluted and "clean" sediments. Pollution of the sediments was detected by the electrical device.

A field study was then conducted over a limited area of Narragansett Bay. Soil sample pollution levels and formation factor readings were compared with similar data of the same area obtained in November, 1973.

• Higher pollution levels were attended by corresponding decreases in formation factor readings. The changes in sediment pollution were traceable through use of the microlaterolog.

The device proved capable of monitoring marine sediment pollution.

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I. INTRODUCTION

In attempting to obtain marine sediment pollution information without going through the bother of in-situ sediment sampling, electronic methods would seem to be advisable.

Such procedures have been available since the late 1800's and practically adapted in the oil industry since 1927.

A brief review of electrical soil exploration will indicate its value to the problem at hand.

II. ELECTRICAL SOIL EXPLORATION

The electrical resistance of a medium is defined as the voltage drop across the medium divided by the current passing through, or

$$\Omega = \frac{V}{I} \quad (1)$$

where Ω = Resistance
V = Voltage Drop
I = Current

This is, of course, Ohm's Law and the units of resistance are ohms. The resistivity of any medium is the capacity of that medium for resisting the electrical flow. The resistivity is actually the total electrical resistance observed when considered with the physical parameters of the medium.

$$R = \Omega \frac{A}{L} \quad (2)$$

where R = Resistivity
 Ω = Resistance (ohms)
L = Length of medium
A = Cross-sectional area of medium

Resistivity is expressed in ohms - unit length. Conductivity of a medium is simply the reciprocal of resistivity. That is to say it is the capacity of a material to conduct electrical flow and has units of mhos - unit length. Mho is the common unit of conductance.

In reviewing literature, this author has found that the electrical characteristics of sediments (particularly rocky strata) have been related to resistivities. Characteristics of solutions, however, have been more

3

frequently expressed by conductivity. Since both physical phases are important to this study, the author has chosen to follow the conductivity convention. However, references to other authors have been kept in their particular conventions for accuracy. It is again pointed out that conductivity, C , is related to resistivity, R , by

$$C = \frac{1}{R} \quad (3)$$

Soil is a three-phase substance. It contains solids in the form of minerals and some organics. Liquids are represented normally by water, and gases usually by water vapor and air. If the soil is located in the marine environment, only two phases, solid and liquid, are present.

Several relationships have been developed relating the ratios of the various phases in a soil. One of these is the porosity. Porosity is defined as the volume of the gaseous and liquid phases (volume of voids) divided by the total volume.

$$\text{Porosity (N)} = \frac{V_{\text{voids}}}{V_{\text{total}}} \quad (4)$$

In the marine environment, the volume of voids is exactly equal to the volume of water. Then

$$\text{Porosity (N)} = \frac{V_{\text{water}}}{V_{\text{total}}} \quad (5)$$

The importance of this ratio will become apparent.

Electrical soil exploration techniques date back

to the 1880's. However, the techniques were first used with confidence by the oil industry in 1927. Here, the resistivity methods, known as well logging, are of use in determining the porosity of the soil around a well, and the conductivity and composition of any interstitial fluids. Wyllie and Gregory (1), Wenner (2), Nettleton (3), and Dobrin (4) review these efforts in depth.

Well logging methods have been of particular interest to individuals studying marine sediments due to the similarity of conditions under which the equipment performs. The probes, or electrodes, must be totally submerged (in drilling mud or sea water) and are subject to quite high pressures.

In 1962, Dakhnov (5) attempted to summarize all the factors effecting electrical resistivity in a sediment. He developed the equation:

$$R_s = f_1(c)f_2(N)f_3(S)f_4(t)f_5(Q)f_6(R_m)f_7(R_w) \quad (6)$$

where: R_s = resistivity of sediment

C = amount clay/silt in sediment

N = porosity

S = degree of saturation

t = temperature

Q = cation exchange capacity

R_m = resistivity of soil mineral

R_w = resistivity of interstitial water

A brief analysis of the above seven factors influencing

sediment resistivity will indicate how the equation may be simplified.

1. S, degree of saturation - For any sediment which is fully-submerged, the sample is 100% saturated. This factor would be equal to one in the above equation.
2. t, temperature - Resistivity is a temperature-dependent quantity. However, if all sample readings are corrected to a standard temperature, the temperature effect is nullified. Such a correction is performed by using the equation

$$R(25) = R(t) [1 + C_t(t - 25^\circ \text{C})] \quad (7)$$

where: $R(25)$ = resistivity at 25°C

$R(t)$ = resistivity measured at temperature, t

C_t = temperature coefficient of resistivity, usually 2.5%/degree centigrade

3. R_m , resistivity of soil mineral

Table 1 is a composite listing of the resistivities of various minerals, metals, and several solutions taken from Dakhnov (5) and Weast (6). It is most interesting to note that with the exception of graphite, coal, and some relatively rare minerals, the resistivities of the minerals are several orders of magnitude higher than those for the metals and solutions. In solids, current is passed along by electrons which can break free from the solid. Free ions carry the current in a solution. In view of equations (1) and (2), it

TABLE 1. Resistivities Of Several Minerals, Elements, And Aqueous Solutions

<u>Mineral</u>	<u>Resistivity (ohm-meters)</u>	<u>Elements</u>	<u>Resistivity (ohm-meters)</u>
Anhydrite	10^7 - 10^{10}	Calcium	3.91×10^{-4}
Hematite	10^4 - 10^6	Chromium	12.9×10^{-4}
Graphite	10^{-6} - 10^{-4}	Iron	9.7×10^{-4}
Calcite	10^7 - 10^{12}	Magnesium	4.5×10^{-4}
Sylvite	10^{14} - 10^{15}	Copper	1.7×10^{-4}
Quartz	10^{12} - 10^{14}	Silver	1.6×10^{-4}
Limonite	10^6 - 10^8	Zinc	5.9×10^{-4}
Magnetite	10^{-4} - 10^{-2}	Sodium	4.2×10^{-4}
Marcasite	10^{-2} - 10^2		
Muscovite	10^{11} - 10^{12}		
		<u>Solutions</u>	<u>Resistivity (ohm-meters)</u>
Oil	10^9 - 10^{16}	0.6M NaCl	2×10^{-3}
Pyrite	10^4 - 10^{-1}	1.0M AgNO ₃	1.3×10^{-3}
Clays	10^{11} - 10^{12}	0.125M CuSO ₄	10.7×10^{-3}
Pyrolusite	1-10	0.5M CaCl ₂	1.4×10^{-3}
Sulfur	10^{12} - 10^{15}	0.137M HCL	2.2×10^{-3}
Siderite	10 - 10^3		
Biolite	10^{14} - 10^{15}		
Anthracite	10^{-4} - 10^{-2}		
Bituminous	10^2 - 10^6		

would be expected that the high resistivities of minerals would result from a low source of free electrons. This is exactly the situation. Most minerals, by composition structure, have few free electrons available for transfer. With the basic premise that electricity will follow the path of least resistance, it appears that current flow in a water-soil sediment will travel through the interstitial fluid. Such an analysis has been supported by Dakhnov (5) and Williams (7). The quantity, R_m , may be neglected as long as the several "rare earths" are not present.

4. R_w , resistivity of interstitial water - This factor could significantly influence soil resistivity readings if the interstitial water resistivities were altered from those of the surrounding fluid. Kullenberg (8) and Boyce (9) noted in their respective studies that the salinity of interstitial water in marine sediments varied by less than 2.3% from the salinity of the water overlying the sediment. Similar results were obtained through more theoretical methods by Smirnov (10). The resistivity of interstitial water in a marine sediment may be equated to the resistivity of the water over the sediment, without corrections.
5. Q , cation exchange capacity - All soils have free ions available on the particles' surfaces. The ability of

the soil particles to release these ions is expressed by the quantity of ions available. From Wilun and Starzewski (11):

"The quantity of exchangeable ions expressed in milliequivalents per 100g mass of the dry soil is known as the ion exchange capacity".

Table 2 expresses cation exchange capacity limits.

TABLE 2. Cation Exchange Capacity of Several Soil Types

<u>Soil Type</u>	<u>CEC (meq/100g)</u>
Natural Soil	0 - 40
Kaolinite Clay	3 - 15
Illite Clay	20 - 40
Montmorillonite Clay	60 - 100

Many individuals have analyzed the effect of cation exchange capacity (CEC). Four studies of particular interest were performed by Berg (12), Kermabon (13), Winsauer (14), and Hill and Milburn (15). The studies conducted from 1951 through 1969 separately concluded that if the resistivity of the interstitial water was low (below 80 ohm - cm), cation exchange capacity has no effect. Sea water has a salinity of 35 ppt, which gives a resistivity of 25 ohm - cm. In a marine environment, then, CEC may be ignored.

6. C, clay/silt fraction

The clay/silt fraction in a soil could effect the soil

conductivity in three manners. First, is the cation exchange capacity just discussed. Second, is by providing a greater assortment of particle shapes. Work done by Wyllie and Gregory (1) and Erchul (16) supports the contention that particle shape does not affect resistivity readings. The third possible effect is through grain size distribution. As noted earlier, the higher resistivities of soil minerals cause electrical currents to flow through the interstitial fluid. As the grain size distribution increases and covers a larger variety of particle sizes, the interstitial fluid path becomes longer, thereby increasing resistivity. Dakhnov (5) describes this current path by the term "tortuosity". He defines tortuosity as the ratio of the disturbed current path to the straight line current path created by the physical size of the sample. He further related tortuosity to the resistivities and porosity of the sediment by

$$T = \left(\frac{R_s}{R_w} N \right)^{\frac{1}{2}} \quad (8)$$

For any one soil, the gradation will be constant, and the tortuosity effects between samples should be negligible. For different soil types, tortuosity will affect the readings.

Equation (8) also presents the ratio of sediment resistivity to water resistivity. Although this ratio

shows up in theoretical analyses as early as 1881, it was not until 1942 that it was named. At that time, Archie (17) introduced the term Formation Factor. The formation factor served as a method for normalizing the measured resistivities of saturated soils against the interstitial fluid.

$$FF = \frac{R_s}{R_w} = \frac{C_w}{C_s} \quad (9)$$

where: R_s = resistivity of saturated soil

R_w = resistivity of interstitial water

C_s = conductivity of saturated soil

C_w = conductivity of interstitial water

All other variables being equal, a given saturated soil should give the same formation factor regardless of the conductivity of the interstitial fluid.

Equation (6) has thus been simplified and modified to:

$$\frac{R_s}{R_w} = FF = f_1(c)f_2(N) \quad (10)$$

In 1942, Archie (17) proposed the relation:

$$FF = N^{-m} \quad (11)$$

Winsauer (14) suggested the equation:

$$FF = a N^{-m} \quad (12)$$

For both equations (11) and (12), FF is the formation factor, N the porosity, and "a" and "m" are values obtained from a log-log plot of FF versus N. "a" is the intercept at the 100% porosity point, and

"m" is the slope of the plot. Thus, the Dakhnov equation has been reduced to equation (12) for marine sediments.

The obvious question after considering the above theory is "can it all be practically applied?" In 1972, Erchul (16) proved that the theory did work. In a series of tests, Erchul obtained formation factors at various porosities for thirteen different sediments. By applying linear regression analysis to the data as substituted into the equation

$$\log FF = \log a - m \log N \quad (13)$$

coefficients "a" and "m" could be determined. Figure 1 is a sample of the data presentation. Table 3 is a list of coefficients obtained from the data.

In 1973, Killoy (18) used a microlaterolog resistance pad to measure marine sediment formation factors and predict the porosities using the Erchul coefficients. Extremely good correlations were obtained between the predicted and observed porosities both in the laboratory and in the field.

The microlaterolog resistance pad used by Killoy was developed by Doll of the Schlumberger Well Surveying Corporation (19). The pad consists of a center electrode with three concentric ring electrodes. As used by Killoy, a small current was forced to flow between electrodes A(0) and A(1). Connected instrumentation

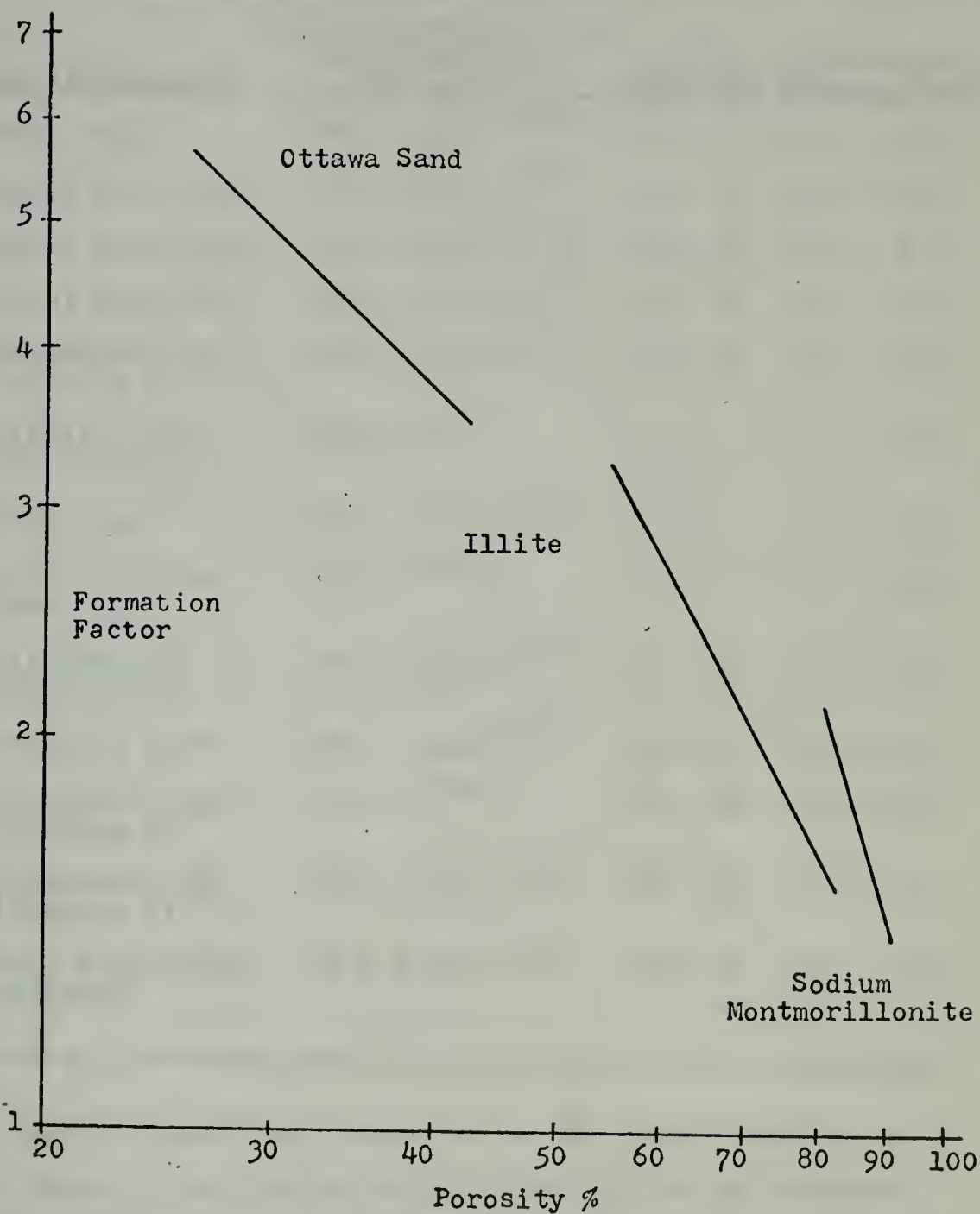


FIGURE 1. Formation Factor - porosity relationships for three soils as done by Erchul (16)

TABLE 3. The Coefficients Of The Model Equation, Porosity Range And Formation Factor Range Of Thirteen Sediments From Erchul (16)

Name of Sediment	Coefficients of the Model Equation* $FF = an^{-m}$	Porosity Range (%)	Formation Factor Range
Ottawa sand	$FF = 1.55 n^{-0.97}$	26 - 43	3.5 - 5.7
Glacial sand (1-a)	$FF = 1.57 n^{-0.96}$	30 - 47	3.2 - 5.0
Glacial sand (1-b)	$FF = 1.35 n^{-1.10}$	31 - 47	3.1 - 4.7
Glacial sand (2)	$FF = 1.45 n^{-1.10}$	31 - 46	3.4 - 5.4
Narragansett Bay (Station C)	$FF = 1.47 n^{-1.20}$	32 - 40	4.3 - 5.7
Kaolinite clay (0.6N NaCl)	$FF = n^{-1.97}$	51 - 92	1.2 - 3.8
Illite clay	$FF = 1.08 n^{-1.82}$	55 - 81	1.6 - 3.3
Montmorillonite clay	$FF = n^{-4.11}$	81 - 96	1.4 - 2.1
Kaolinite clay (Quadrafos)	$FF = 1.05 n^{-1.24}$	41 - 94	1.1 - 3.1
Providence silt	$FF = 1.11 n^{-1.75}$	41 - 62	2.5 - 5.2
Narragansett Bay (Station A)	$FF = n^{-2.22}$	47 - 82	1.5 - 5.0
Narragansett Bay (Station B)	$FF = 1.15 n^{-1.75}$	44 - 74	2.0 - 4.9
Puerto Rico marine sediment	$FF = 1.36 n^{-1.77}$	46 - 74	2.1 - 5.0

*

On double logarithmic paper (m) of the model equation is the slope of the line of best fit and (a) is the intercept of the equation's line with the vertical axis at 100 percent porosity.

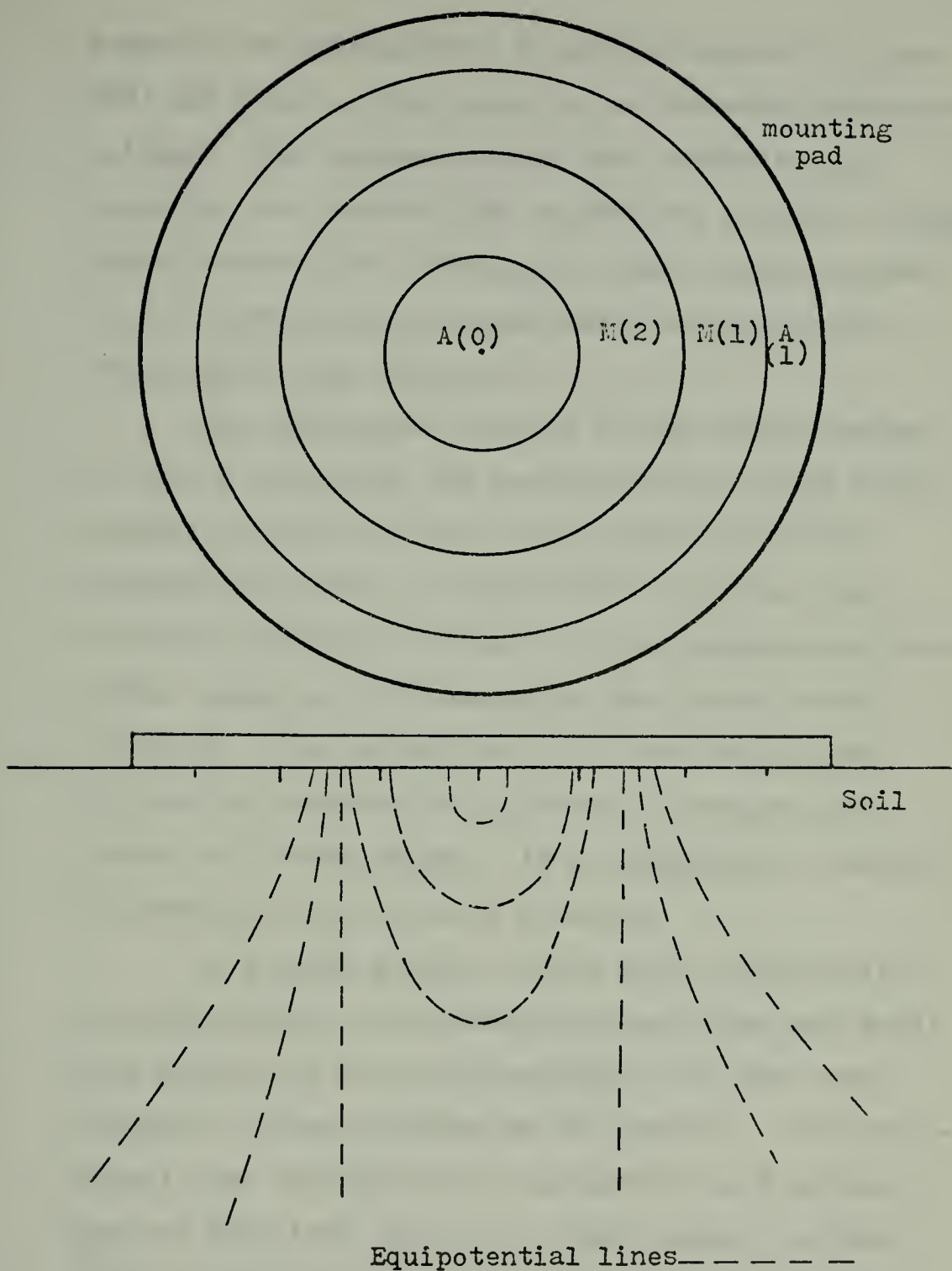


FIGURE 2. Microlaterolog as per Doll (19)

measured the voltage drop across electrodes M(1) and M(2) and compared the result to an internal referenced voltage. The instrumentation then automatically corrected the current flow so that the measured voltage always equaled the referenced voltage. This current flow is then directly proportional to the medium's conductivity (see Figure 2).

One significant benefit of the microlaterolog is that it restricts the sediment volume being tested. Dakhnov (5) and Doll (19) concur that electrical penetration occurs to approximately six times the effective electrode radius. For a microlaterolog this radius would be the diameter of the largest ring electrode. One assumption in all resistivity work is that the material being tested is homogeneous across the tested volume. It is therefore of benefit to restrict this volume if possible.

As a small portion of his study, Killoy (18) introduced three pollutants (oil, gasoline, and soap) into several of his test specimens. He then took formation factor readings on the samples. His conclusions: "the introduction of pollutants such as oil, gas and soap into the water column causes a notable change in formation factor and this can conceivably be used as a pollution indicator".

This study follows that Killoy proposal.

III. POLLUTION IN SOIL

Using a conductivity device of any type to measure soil pollution in a marine sediment would appear to obviously work. If a pollutant altered the conductivity of sea water, it could be detected! Naturally, the formation factor may not be immediately modified, since the conductivities of water and soil could conceivably be altered to the same degree. Yet, if a typical polluting action such as an oil spill is considered, even altering both sea and soil conductivities would be significant. This is because it can be expected that the water would improve in quality faster than the soil. Perhaps nothing more than a change in tides could withdraw a pollutant from the water column. Once a pollutant entered the sediment, however, a slower quality improvement would result. It is at this point that formation factor readings would be valuable and indicative of soil problems.

Probably the first step in analyzing sediment pollution processes is to look at what this author feels are the dispersion characteristics of the pollutant. The solubility of the pollutant together with its specific gravity tend to indicate the mechanics of the situation. A highly-refined soil may be so insoluble in water that it takes years before it can affect a conductivity change. A soap, on the other hand, may dissolve and disperse throughout the water column immediately. A similar analysis can be

made of specific gravities. Pure mercury will most certainly affect the surface of a marine sediment even if its presence is never detected in the water! It is the characteristics, physical as well as electrical, of a pollutant which tend to make conductivity readings a successful detection or monitoring device.

The next consideration must be the physio-chemical phenomena of soils. On most natural soils, there exists little affinity between soil particles and other soil particles or between soil particles and other matter. Recalling Table 2, the cation exchange capacity for most natural soils is between zero and forty milliequivalents per 100g of soil. Therefore, for most granular samples, the pollutants will travel through the soil following the mechanics as mentioned above.

Referring back to the Dakhnov equation (6), the assumption that the resistivity of interstitial water is equal to that of the water just above the sediment is no longer practical. A change in formation factor will result. However, for granular samples the other assumptions still remain valid. These processes become much more complex for clays.

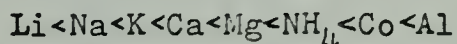
For clays, the assumptions regarding cation exchange capacity are no longer valid when pollutants are considered.

The charge on clay particles causes water dipoles to be attracted to them. These molecules form a double layer around the clay particles. This process is explained by the Gouy - Chapman Double Layer Theory. For a saturated soil, the pore water electrical characteristics never really "touch" the clay particles, since the particles are surrounded by the bound water layers. Wilun and Starzewski (11) say:

"The thickness of the double layer, and of the adsorbed water layer, depends upon the chemical composition of the solid particles and on the valency of the adsorbed ions. The type of adsorbed cations has a very significant influence on the behavior of the soil".

The ability of the soil to give up the electrical charges on their particles is the cation exchange capacity, discussed in Chapter II. Since the cations causing the double layer are the same ones being considered by CEC, a pollutant which effects the electron balances in a clay will certainly have an impact on the sediment.

Grim (20) states that CEC is dependent upon the concentration of clay, the nature of cations, and the concentration of cations. Grim also presents an introduction to the lyotropic series. This series lists the replacing power of several common ions. One small phase:



From the series, it would be expected that ammonium would more easily replace sodium than vice versa. Grim cautions,

however, that the series can be altered by increased concentration of any given ion, and by changing the clays being considered.

Van Olphen (21) and Rebinder (22) describe research which has been done on drilling muds. Both studies provide details of the effect of organics on various clay suspensions. Several of the observations:

1. Hydrocarbon chains can attach themselves to the clay particle surface and displace adsorbed water molecules.
2. Many organic compounds with a dipole character are adsorbed on clay in the same manner as water.
3. Organic molecules of alcohols, glycols, or amines have been observed to displace interlayer water in montmorillonites.
4. The double layer of several clays was compressed when the dielectric constant of the surrounding solution was decreased by the addition of water-miscible organic solvents.
5. Adsorption of organic cations can magnify the CEC of a clay by as much as two and one-half times.
6. Some amine salts in low concentration can decrease the bound water layers; yet when concentrations are increased can actually cause the layers to swell.

Pollutants have a very definite effect on formation factors. For a predominantly granular soil, the effect will manifest itself through the resistivity of the pore

water and also the cation exchange capacity.

This brief analysis indicates the difficulties attendant with attempting to predict the effect of a pollutant on any soil, particularly a clay. For that reason, the balance of this study will be carried out under qualitative and empirical methods. The results of the polluting mechanisms will be the predominant concern.

IV. LABORATORY TESTING

Equipment

All instrumentation was identical to that used by Killoy. Three pieces of equipment composed the instrumentation: (1) a conductivity signal conditioner, (2) a digital volt meter, and (3) a microlaterolog pad.

The conductivity signal conditioner was Honeywell, Inc. model number 552022 - 2002 - 103 - 003, with a range of 0 - 60,000 micromhos - cm. The principle of operation was previously discussed in Chapter II. Briefly, the conditioner controls a current across a multi-electrode conductivity array so that a measured voltage drop is equal to an internal fixed reference voltage. The current flow is, therefore, directly proportional to measured conductivity. The indicated signal conditioner also has the capability to compensate all conductivity readings to 25° C. To perform this function a Yellow Springs Instrument Company 100 ohm thermistor was attached to the probe and connected to the instrument. The Honeywell conditioner provides output in three different signal forms. A meter on the instrument shows conductivity in mhos - cm. Internal jacks also provide access to output in VDC or in VAC. The author chose the VDC output and connected the same to a digital voltmeter. This yielded more precise values than could be read from the Honeywell meter.

The voltmeter used was a Non-Linear System Digital Voltmeter Series MX-3. The lowest range of 0 - 20.00 volts was used.

For this phase of the study, the microlaterolog built by Killoy was used. However, early in the testing a short-circuit on the pad face required that the sensor be rebuilt. For information purposes, a brief description of the microlaterolog follows. Four electrodes were on the face of an acrylic plastic pad. There was a center point electrode and three concentric ring electrodes of radii $1/4$, $1/2$, and $3/4$ inches. Electrodes were formed from American Enka Corporation Kynar 16AWG wire with resistance of 6.89×10^{-4} ohms per centimeter. The electrodes were held to the face using epoxy, and leads were passed through the plastic to the rear of the pad. The thermistor was attached to the side of the pad and its leads were also brought to the rear.

A $1/2$ -inch diameter acrylic tube was epoxied to the rear of the pad and all leads passed up through the tube to the signal conditioner. A small amount of lead shot and epoxy was placed in the tube to waterproof all electrodes and to provide ballast. Killoy (18) estimated that the microlaterolog would penetrate approximately 4.5 inches into the sediment. Figures 3, 4, and 5 show the microlaterolog and instrumentation.

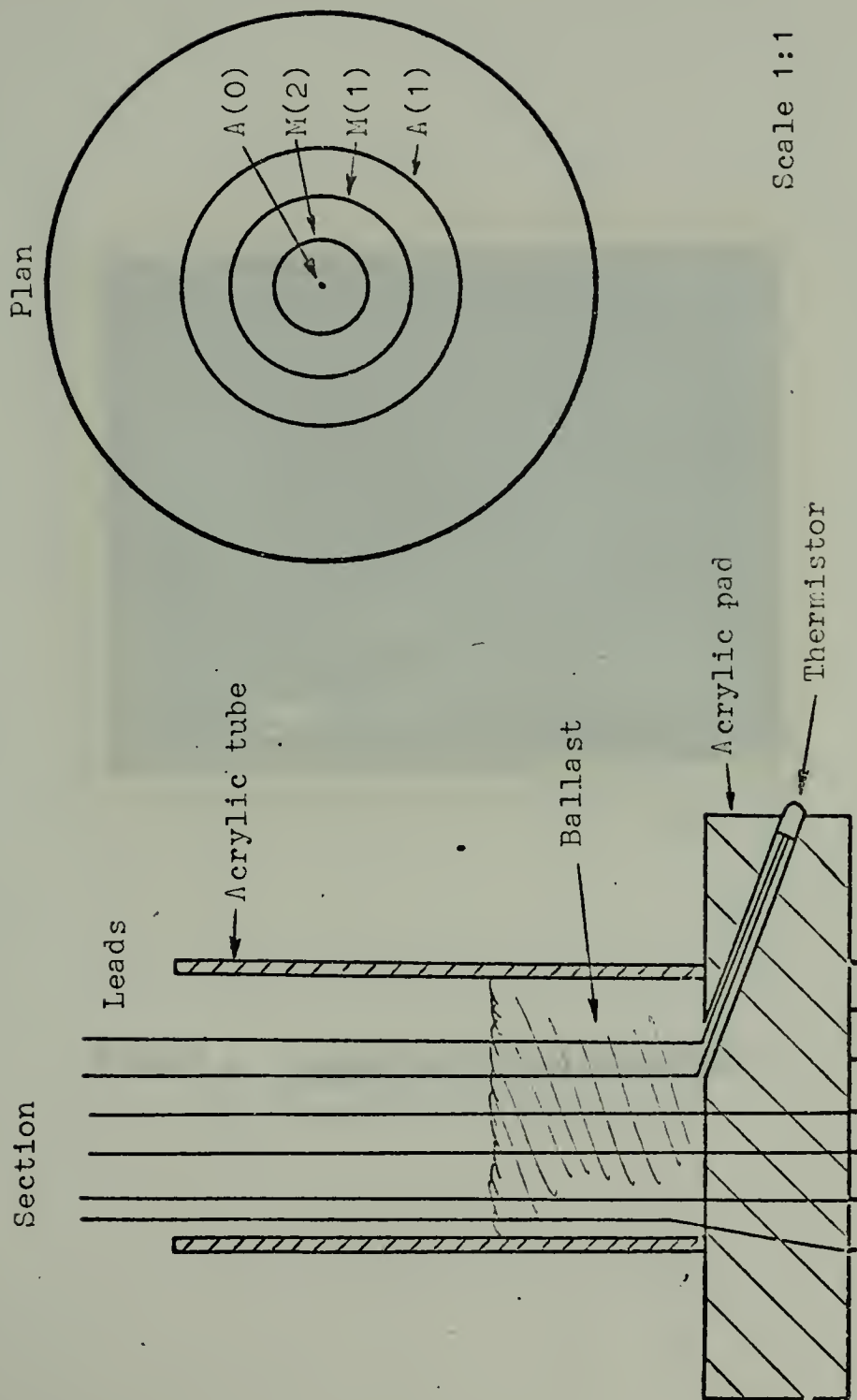


FIGURE 3. Laboratory Microlatrolor Pad After Killoy (18)

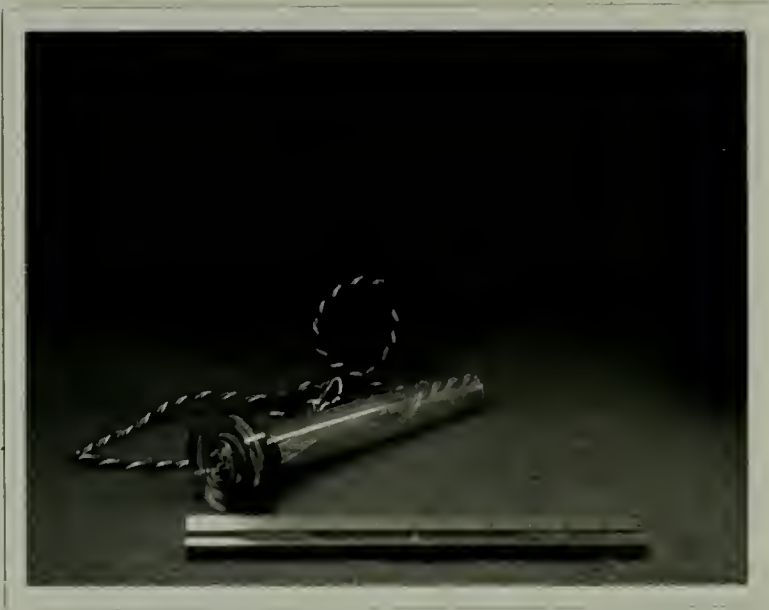


FIGURE 4. Laboratory Microlaterolog

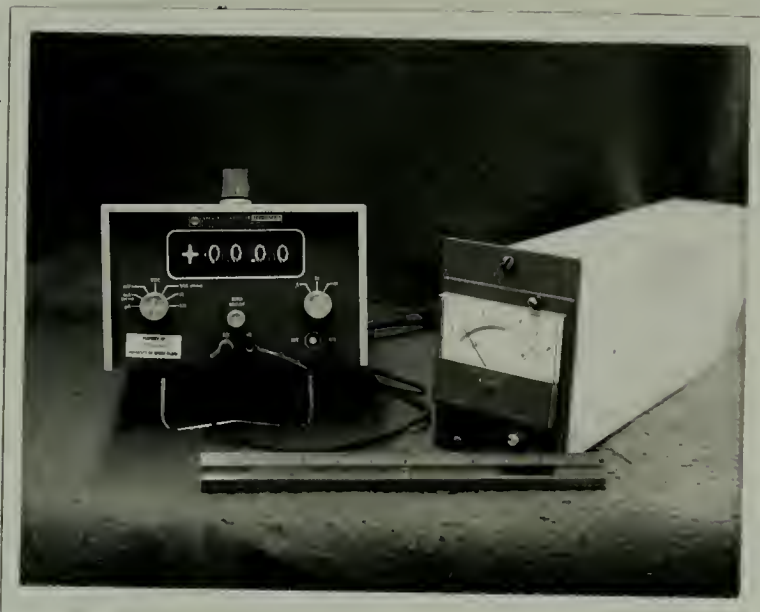


FIGURE 5. Instrumentation

The instrumentation when operational provided conductivity readings in volts to the nearest 0.05 volts. This was an accuracy of 1%.

Appendix 1 contains manufacturer's information concerning the Honeywell Conductivity Signal Conditioner and YSI Thermistor.

Laboratory Testing Procedures

Three different soil types were chosen for study. These were (1) Ottawa Sand (soiltest type CN-501 Density Sand), (2) Sodium Montmorillonite Clay (Black Hills Bentonite from International Minerals and Chemical Corporation), and (3) Illite Clay (Grundite from A. P. Green Refractories Company).

Ottawa sand was chosen to provide a granular sample. Sodium montmorillonite was chosen because it is homoionic to the sodium ion. It was felt that this electrical configuration might provide some interesting pollution phenomena. Finally, Illite was chosen due to its predominance on both land and in the sea.

The physical properties of the three samples were determined by this author and are listed in Table 4.

TABLE 4. Sediment Classification

<u>Sediment</u>	<u>Sediment Classification</u>			<u>Specific Gravity</u>
	<u>% Sand</u>	<u>% Silt</u>	<u>% Clay</u>	
Ottawa Sand	100	-	-	2.65
Sodium Montmorillonite	10	10	80	2.73
Illite	8	52	40	2.78

All samples were sedimented in four-liter Pyrex beakers. The beakers were first partially filled with 0.6 normal sodium chloride solution. This approximated, electrically, natural sea water conductivity. The various soils were then gradually shaken into the "sea water" and allowed to settle. Depending upon the type of soil, one of two actions was then performed. For the clays, the sedimented samples were periodically stirred to form a slurry. This was done to minimize air entrapment and insure a saturated sediment. For the granular samples of Ottawa Sand, a certain degree of sample vibration was performed to decrease porosity. This is discussed in depth in several following paragraphs.

While the sedimentation process was occurring, careful note was taken of the weight of soil being utilized. This weight divided by the soil specific gravity (previously obtained) yields the volume of soil being sedimented. After sedimentation had been completed, the volume of the sample could be estimated from the graduated markings on the sides of the beakers. The difference between the two volumes (volume of sample minus volume of soil) is defined as the volume of voids. It, therefore, became relatively easy to obtain the porosity for each soil sample.

It was desired to at least consider the pollution effects on the soil with a change in porosity. Early in

this study it became apparent that any reasonable attempt to control the clays' porosities would be fruitless.

Following the sedimentation procedures, both clays settled to a nearly constant porosity. That is to say that all illite samples naturally settled to a porosity of 65%; the sodium montmorillonite to 86%. Various methods of tamping or consolidating were attempted, but with no success. It was, therefore, decided that all studies of varying porosity would, by necessity, be carried out upon the Ottawa Sand.

Two samples of the Ottawa Sand were prepared. One had as large a porosity as could be attained through natural sedimentation. The second sample was vibrated until its volume in the beaker had been reduced to as low a point as it would go. The vibrator was composed of one Skil Uni-Lectric Flexible Shaft 10 amp Pencil vibrator, one Superior Electric Powerstat Variable Autotransformer (0 - 140 volts), two 0.75"-thick rubber bridge pads, and some miscellaneous lumber and screws. In practice, the one-inch vibrator slid under the rubber pads, within a wooden frame. The beaker containing the sample was then placed on the pads. As the variac setting was increased, vibration to the beaker (and soil) was increased. Figure 6 illustrates the vibration apparatus. It was discovered that a setting of 35% on the variac provided maximum sand settling in about two minutes.

There now existed four different samples for each

pollution run: one dense Ottawa Sand, one loose Ottawa Sand, sodium montmorillonite, and illite.

As a next step, the microlaterolog was calibrated. When routinely measuring formation factors, it is not particularly important to know what the conductivity reading of the water or soil relates to in mhos, since the formation factor is a dimensionless number. However, for this study, the author desired to monitor not only any changes in formation factor, but also the conductivity changes which altered the formation factor. Four calibration solutions of 0.1 N, 0.5 N, 0.6 N, and 1.0 N were carefully prepared from sodium chloride and distilled water. Using the absolute conductivity values for each solution from Weast (6), it became quite easy to adjust the signal conditioner over its output range of 0 - 10 volts. In this manner, the laboratory probe and field probe were calibrated. Figure 7 provides the joint calibration curves.

To insure accuracy, the laboratory probe was calibrated weekly or sooner if the conductivity values were suspect. Calibration solutions were carefully maintained, and reviewed at least monthly. All conductivities have been presented in voltages. Conversions can be made from Figure 7.

Prior to commencing any pollution work, it was absolutely necessary to obtain a meaningful correlation



FIGURE 6. Vibration Apparatus

between the Erchul formation factor coefficients (Table 3), the Killoy microlaterolog arrangement, and this investigator's choice of soils.

A complete set of four samples (two sands, one sodium montmorillonite, one illite) were sedimented and allowed to naturally consolidate. One sand was then vibrated to "maximum" density. Using the weight-volume relationships previously discussed, porosities for the four samples were computed. These porosities were then used in the equation

$$F = a N^{-m} \quad (12)$$

with the values of "a" and "m" from the Erchul work for the given soils. This provided a predicted formation factor.

Formation factors were then obtained using the microlaterolog over a ten-day period. Statistically relevant values were calculated using the median and range as presented by Dean and Dixon (23). Table 5 summarizes the results.

A brief discussion of the confidence intervals is in order. The volume of the sample in the beaker could only be read to \pm 50 cc. When run through the porosity calculations this created an error of one percentage point of porosity. This error carried through on the predicted formation factors to yield the attendant error in those values. Errors for the observed formation factors were the result of the statistical analysis as per the Dean and Dixon presentation.

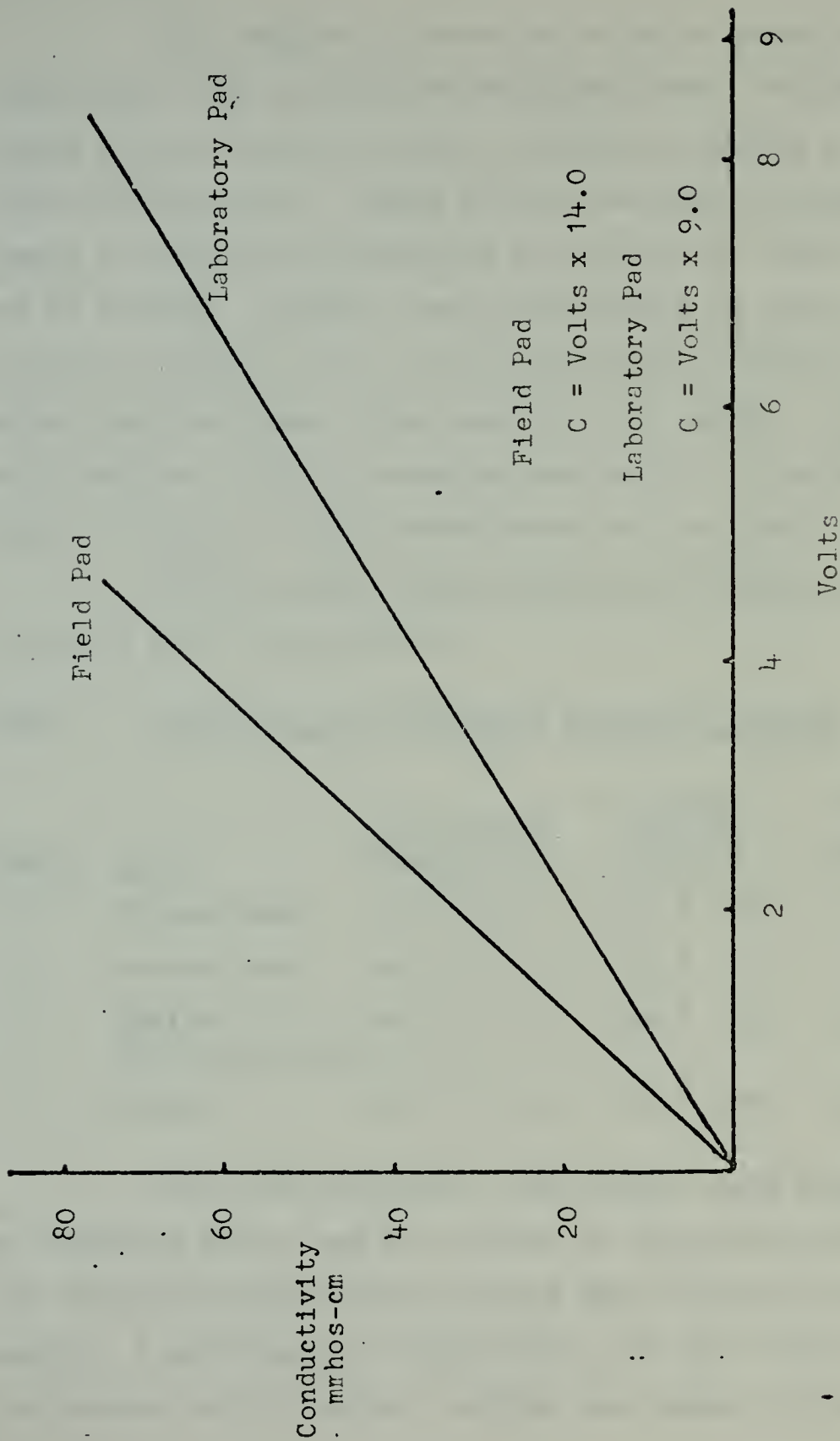


FIGURE 7. Calibration Curves

All samples correlate quite well; sands best, illite next, and sodium montmorillonite last. The larger spread in clay values is quite possibly the result of bottom interferences. Every attempt was made to secure a sample of sufficient depth that the electrical field would not be altered. However, the clays offered so little bearing capacity, even to the light-weight laboratory probe, that the probe often sank into the sample. Since the electrical field extended approximately 4.5 inches below the probe, bottom interference was, at times, possible.

With a rather good correlation obtained, pollution work could now progress.

TABLE 5. Predicted And Calculated Formation Factors

<u>Sample</u>	<u>Soil</u>	<u>Calculated Porosity %</u>	<u>Formation Factor Predicted</u>	<u>Formation Factor Observed</u>
1	Ottawa Sand	34.2 \pm 1.0	4.39 \pm .13	4.37 \pm .11
2	Ottawa Sand	40.9 \pm 1.0	3.69 \pm .13	3.78 \pm .10
3	Sodium Montmorillonite	86.5 \pm 1.0	1.80 \pm .13	1.53 \pm .01
4	Illite	65.0 \pm 1.0	2.36 \pm .07	2.20 \pm .10

For each pollutant, four samples were sedimented as described above, and the "clean" or unpolluted voltages and formation factors were verified with the Erchul coefficients. A pollutant, in liquid form, was then poured into the sample, and electrical readings were taken for approxi-

mately ten days. At that time an additional pollution dose of the same pollutant equal to the initial, was added. The readings were continued for another five days. Data from each pollutant includes pollution concentration, voltages of the soil and interstitial water, and formation factors, compared against time (in days).

A University of Rhode Island Computer Library Program, "Statpack", offers several numerical analyses for statistical information. The author used the program for many of the routine transformations needed in solving the Erchul equations. The Vertical Line Plot analysis proved to be a most convenient format for presenting results of the pollution analysis.

Data and Results

1. The first pollutant chosen to study was a common laundry soap, "Cold Water All", manufactured by Lever Brothers. A solution of soap and tap water was mixed according to label directions. Twelve milliliters of this solution was then poured into each liter of "sea water" above the sediments. Final soap concentration in the beakers was approximately 30 ppm. Readings were taken for five days and then an additional pollution dose was added, bringing soap levels to 60 ppm.

Killoy (18) in his pollution experiments had also used "Cold Water All", although his concentrations are not clear. Over a two-week period he noticed a decrease in the conductivities of water and a slight increase in soil conductivities.

Results are presented in Figures 8, 9, 10, and 11. All four samples clearly show a decrease in water conductivity corresponding to the dosages of soap. Soil conductivities are not nearly as conclusive. Illite demonstrates a definite decrease in conductivity during the entire test. Final illite values have decreased 30% from initial readings. Montmorillonite, after the initial soap dosage, exhibits similar characteristics. However, over time the effect decreases such that final conductivity values are nearly identical to the initial values.

Both sands behave nearly identically to the montmorillonite; values decrease rapidly at first, then gradually return to initial values.

From the information, an interesting trend is observed. The soap effect tends to deteriorate with time. This is quite obvious in all four water readings, and also in all but one (illite) of the soil readings. Perhaps manufacturers' claims of biodegradeable soaps have some validity.

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.48	1.25	4.39
2	5.53	1.30	4.28
3	5.47	1.25	4.37
4	5.32	1.15	4.63
6	5.25	1.13	4.65
7	5.46	1.14	4.76
8	5.52	1.14	4.86
9	5.49	1.17	4.69
10	5.35	1.16	4.57
15	5.44	1.29	4.21
16	5.50	1.30	4.16

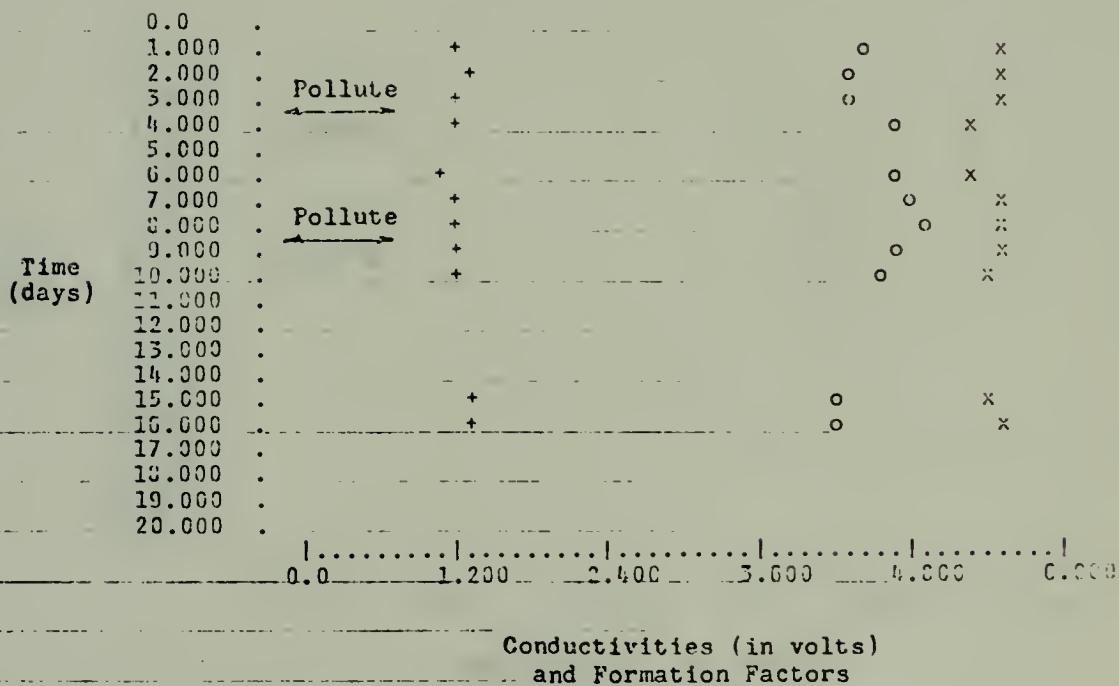


FIGURE 8. Soap in Ottawa Sand (porosity - 34.2%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.42	1.50	3.57
2	5.53	1.47	3.78
3	5.42	1.41	3.86
4	5.30	1.30	4.07
6	5.24	1.24	4.23
7	5.44	1.27	4.30
8	5.53	1.27	4.36
9	5.49	1.29	4.26
10	5.37	1.25	4.29
15	5.40	1.38	3.90
16	5.50	1.42	3.87

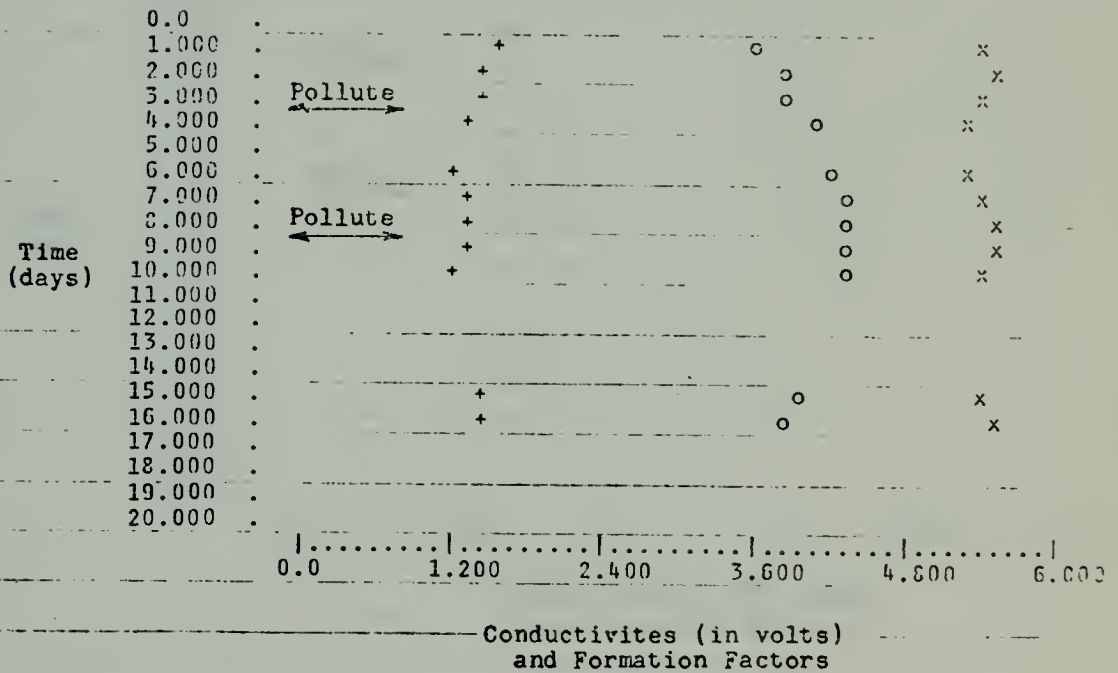


FIGURE 9. Soap in Ottawa Sand (porosity - 40.9%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.80	3.80	1.53
2	5.85	3.82	1.52
3	5.80	3.77	1.52
4	5.56	3.63	1.53
6	5.67	3.67	1.54
7	5.73	3.70	1.55
8	5.90	3.71	1.58
9	5.91	3.90	1.52
10	5.78	3.74	1.55
15	5.83	3.81	1.54
16	5.92	3.78	1.57

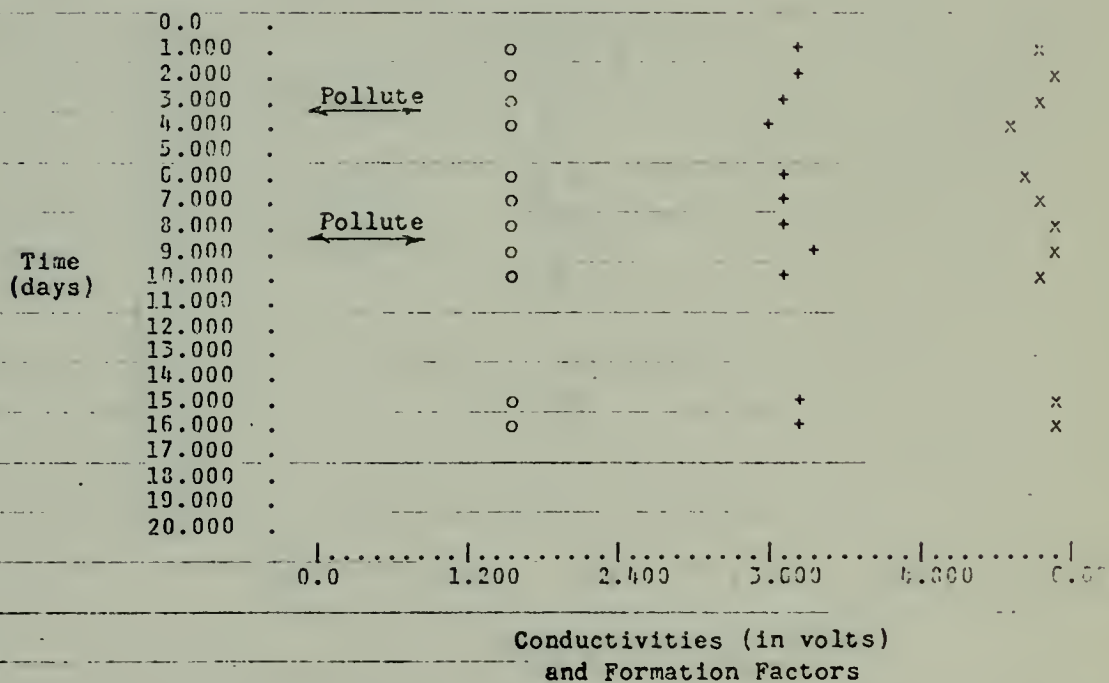


FIGURE 10. Soap in Sodium Montmorillonite (porosity - 86.3%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.57	3.00	2.18
2	6.20	2.90	2.15
3	6.14	2.75	2.26
4	5.87	2.66	2.21
6	5.98	2.58	2.28
7	6.04	2.69	2.24
8	6.12	2.53	2.35
9	6.10	2.50	2.44
10	6.00	2.51	2.39
15	6.27	2.56	2.40
16	6.13	2.65	2.31

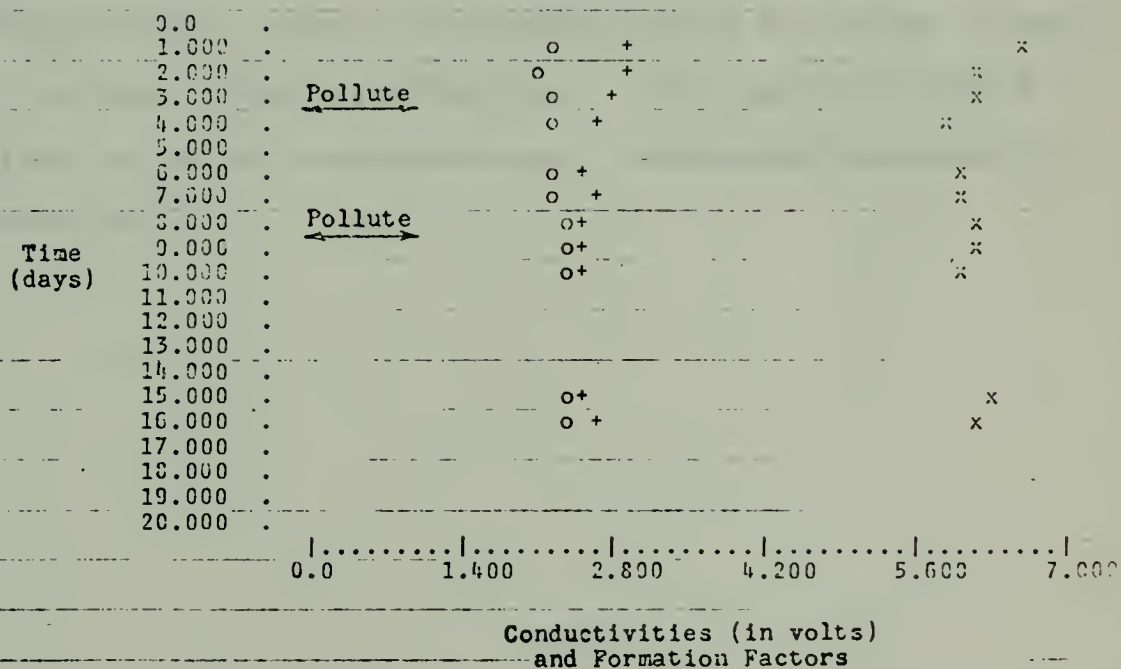


FIGURE 11. Soap in Illite (porosity - 65.0%)

2. Figures 12 through 15 exhibit the effects of zinc on the soil samples. This is one of two heavy metals investigated in this study.

A solution of zinc chloride and distilled water was mixed. This solution was then diluted so that its final concentration in the free water over the samples was 60 ppm of zinc. This concentration was increased to 120 ppm after one week.

The zinc appears to initially decrease the conductivities of all waters. Over the testing period, the conductivities of water generally returned to the initial values. The soil readings began to become affected as the water readings stabilized. Both sands exhibited a slight increase in conductivity. Both clays decreased in conductivity.

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil(+)	
1	5.48	1.25	4.45
2	5.50	1.27	4.35
3	5.52	1.25	4.40
4	5.41	1.17	4.62
6	5.42	1.17	4.66
7	5.50	1.19	4.61
8	5.52	1.23	4.44
9	5.51	1.29	4.27
10	5.50	1.32	4.17
15	5.50	1.33	4.14
16	5.50	1.32	4.16

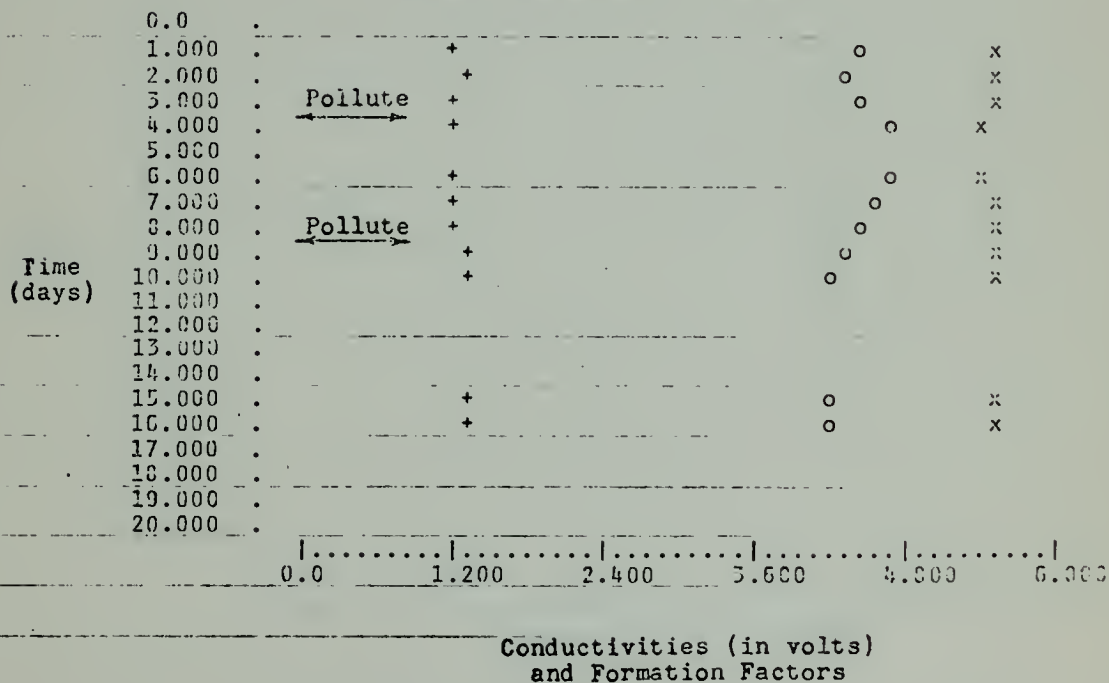


FIGURE 12. Zinc in Ottawa Sand (porosity - 36.4%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.48	1.34	4.09
2	5.52	1.34	4.14
3	5.53	1.37	4.04
4	5.40	1.30	4.15
6	5.40	1.30	4.16
7	5.49	1.32	4.17
8	5.50	1.30	4.19
9	5.51	1.30	4.24
10	5.50	1.38	4.02
15	5.52	1.40	3.94
16	5.49	1.41	3.89

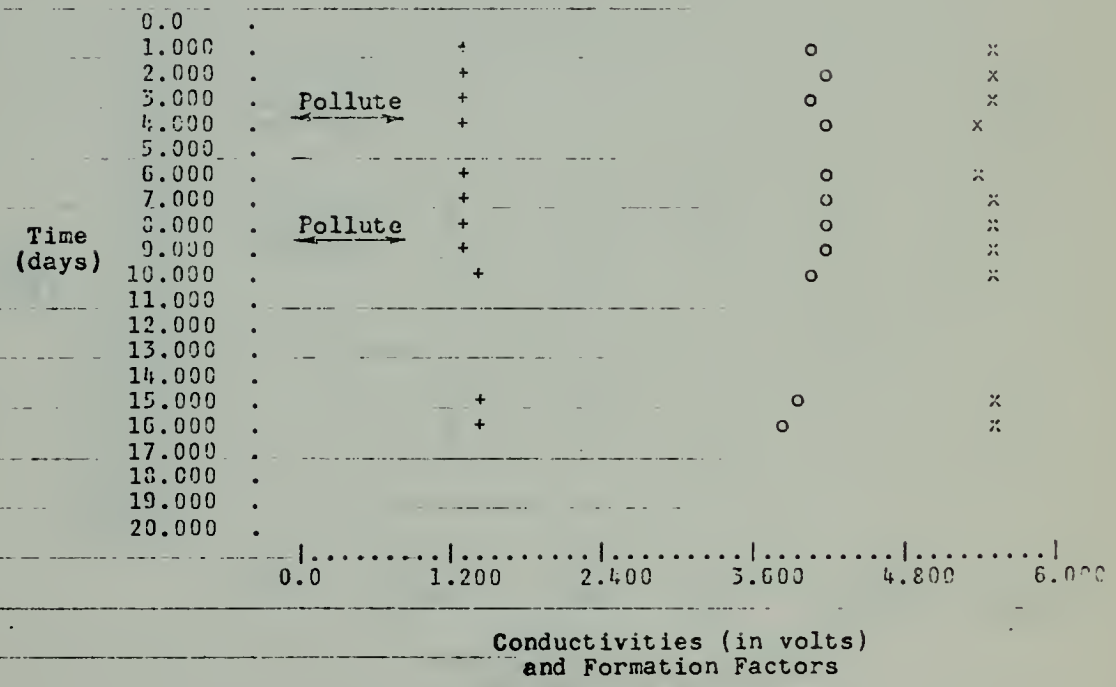


FIGURE 13. Zinc in Ottawa Sand (porosity - 39.1%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.76	3.87	1.50
2	5.94	3.83	1.55
3	5.97	3.82	1.56
4	5.77	3.67	1.57
6	5.67	3.58	1.58
7	5.74	3.64	1.59
8	5.54	3.44	1.61
9	5.86	3.80	1.54
10	5.84	3.78	1.56
15	5.93	3.67	1.60
16	5.92	3.73	1.61

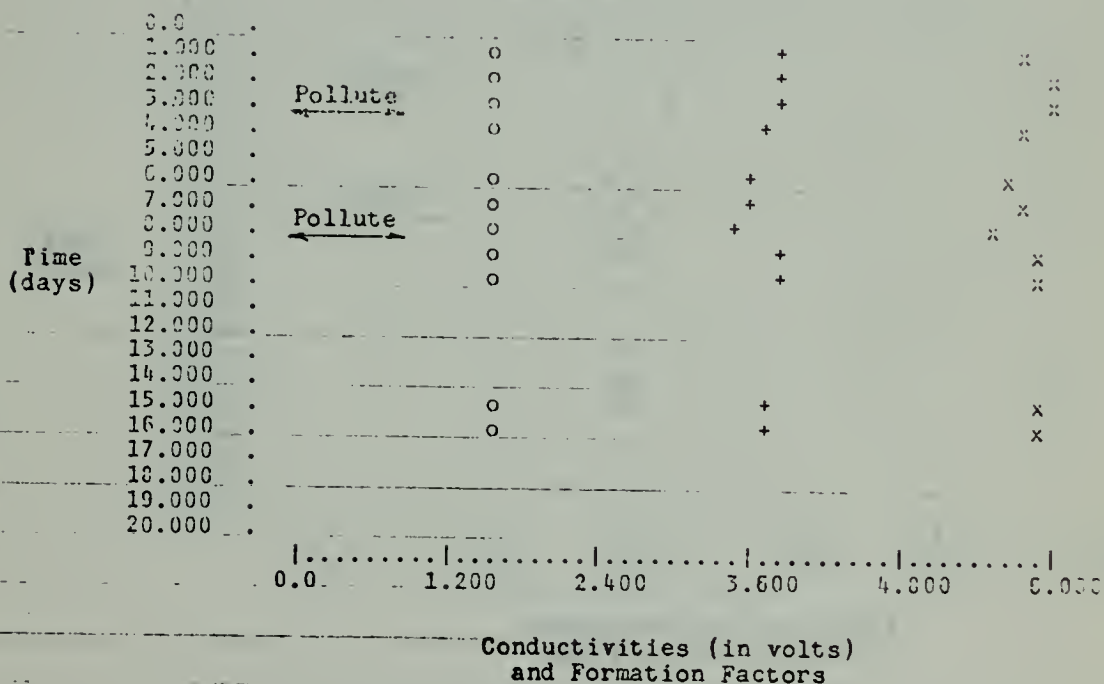


FIGURE 14. Zinc in Sodium Montmorillonite (porosity - 86.9%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.43	3.12	2.06
2	6.14	3.03	2.08
3	6.10	2.80	2.19
4	6.18	2.82	2.19
6	6.18	2.74	2.26
7	6.30	2.77	2.29
8	6.17	2.53	2.44
9	6.19	2.60	2.38
10	5.87	2.40	2.45
15	6.28	2.58	2.42
16	6.24	2.56	2.44

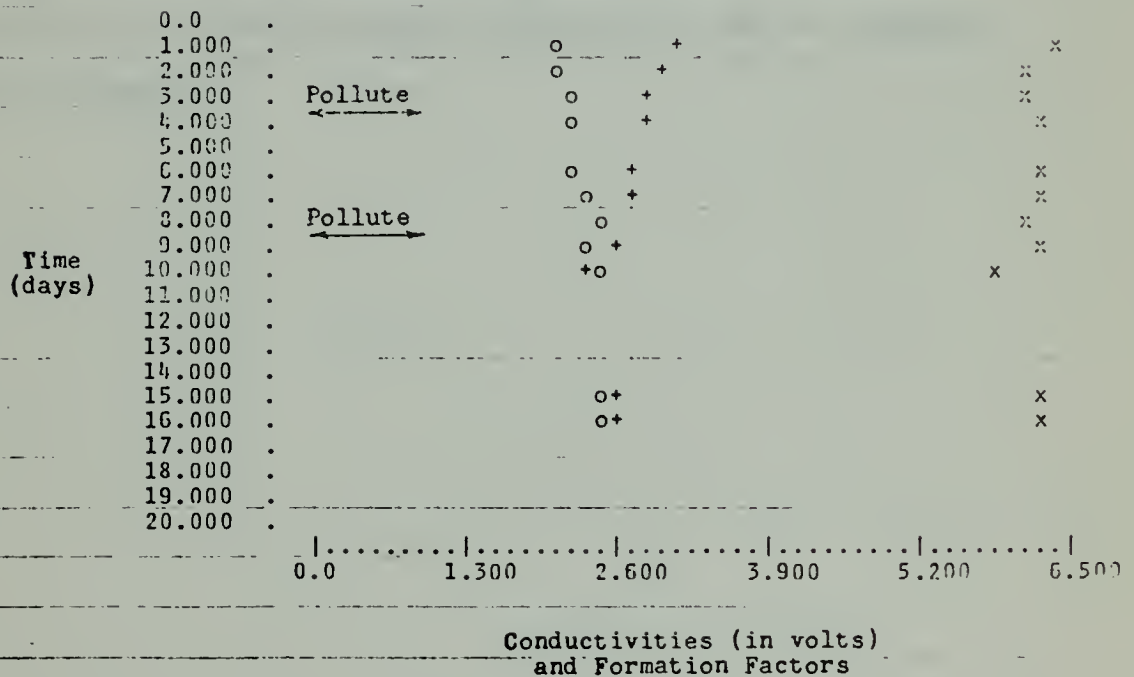


FIGURE 15. Zinc in Illite (porosity - 64.3%)

3. A dextrose solution was chosen to pollute the next batch of soils. Initial concentration of 180 ppm was chosen, since the solubility of sugar was thought to decrease any effect the sugar might have on the soils. After nine days, the concentration was increased to 360 ppm. Results follow in Figures 16 through 19.

No conclusive observation can be made regarding conductivity changes in the water column. Slight variations are evident, but all fall within instrument error values. The sugar does appear to slightly increase soil values in the sands, while slightly decreasing those values in the clays. No overwhelming conclusions can be reached on this pollutant.

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.45	1.20	4.44
3	5.42	1.20	4.44
4	5.50	1.20	4.63
5	5.42	1.20	4.60
6	5.50	1.21	4.55
7	5.42	1.20	4.48
12	5.50	1.30	4.27
13	5.48	1.30	4.21
14	5.46	1.35	4.04
18	5.42	1.42	3.81
19	5.40	1.38	3.93
20	5.42	1.35	4.03

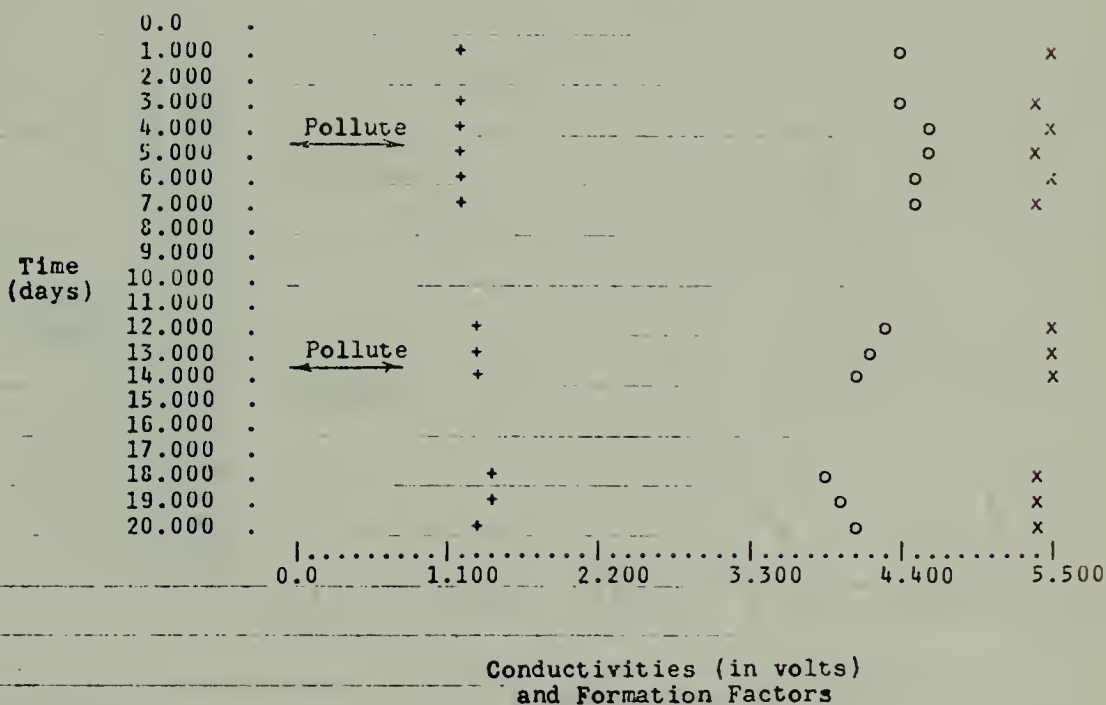


FIGURE 16. Dextrose in Ottawa Sand (porosity - 37.8%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.42	1.44	3.75
3	5.41	1.42	3.86
4	5.51	1.35	4.09
5	5.42	1.35	4.02
6	5.48	1.35	4.06
7	5.40	1.30	4.18
12	5.50	1.40	3.91
13	5.48	1.39	3.93
14	5.45	1.48	3.68
18	5.42	1.52	3.57
19	5.40	1.47	3.67
20	5.40	1.44	3.75

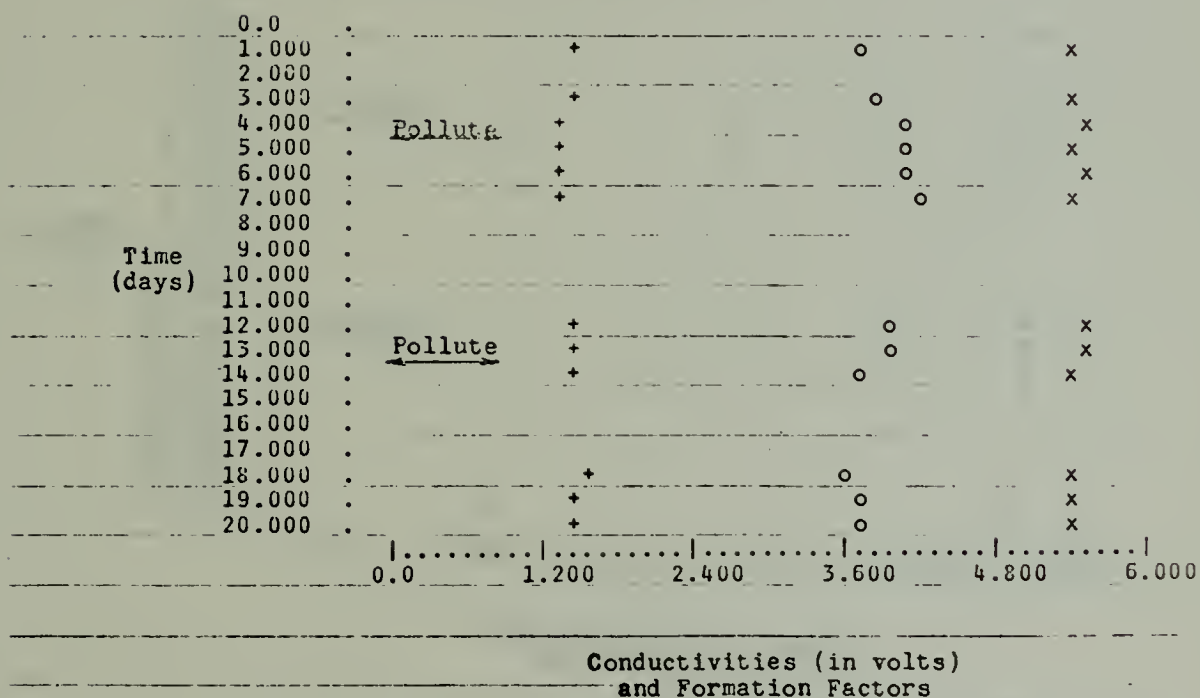


FIGURE 17. Dextrose in Ottawa Sand (porosity - 40.9%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.80	3.62	1.60
3	5.86	3.69	1.60
4	6.08	3.60	1.67
5	5.93	3.62	1.64
6	5.95	3.66	1.63
7	5.98	3.54	1.67
12	6.14	3.74	1.64
13	6.06	3.76	1.61
14	6.08	3.67	1.66
18	5.94	3.77	1.58
19	5.97	3.70	1.61
20	5.88	3.67	1.60

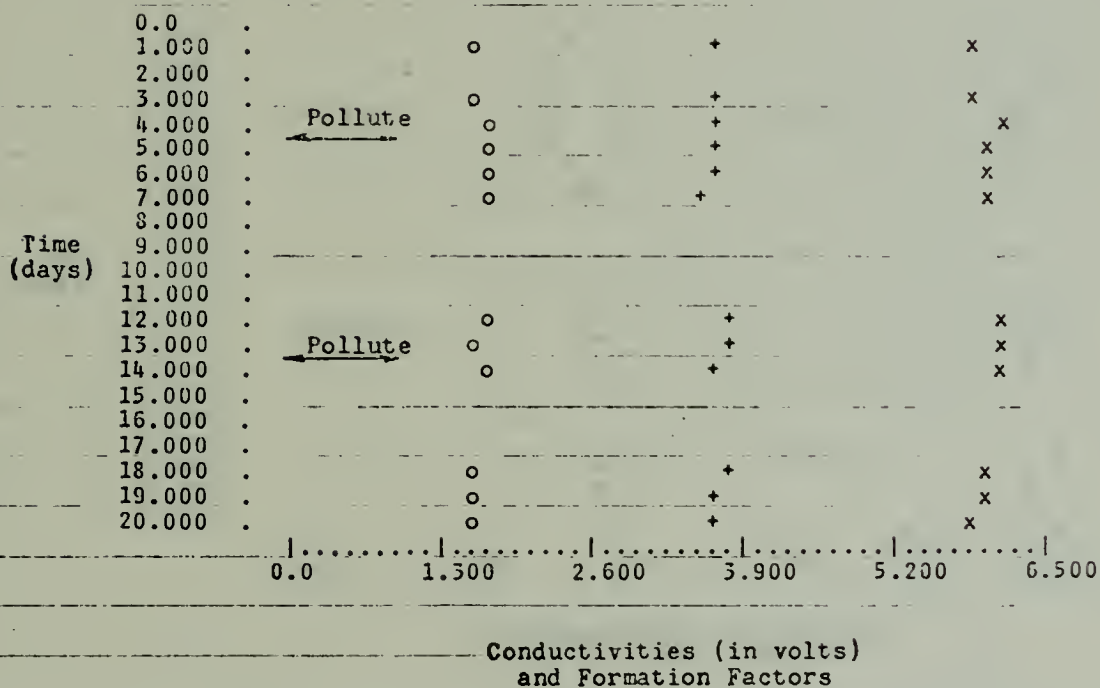


FIGURE 18. Dextrose in Sodium Montmorillonite (porosity - 86.3%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.26	2.66	2.36
3	6.44	2.87	2.24
4	6.28	2.76	2.22
5	6.21	2.76	2.24
6	6.26	2.70	2.32
7	6.27	2.59	2.42
12	6.31	2.56	2.44
13	6.33	2.56	2.47
14	6.30	2.47	2.54
18	6.50	2.50	2.59
19	6.30	2.41	2.61
20	6.33	2.33	2.72

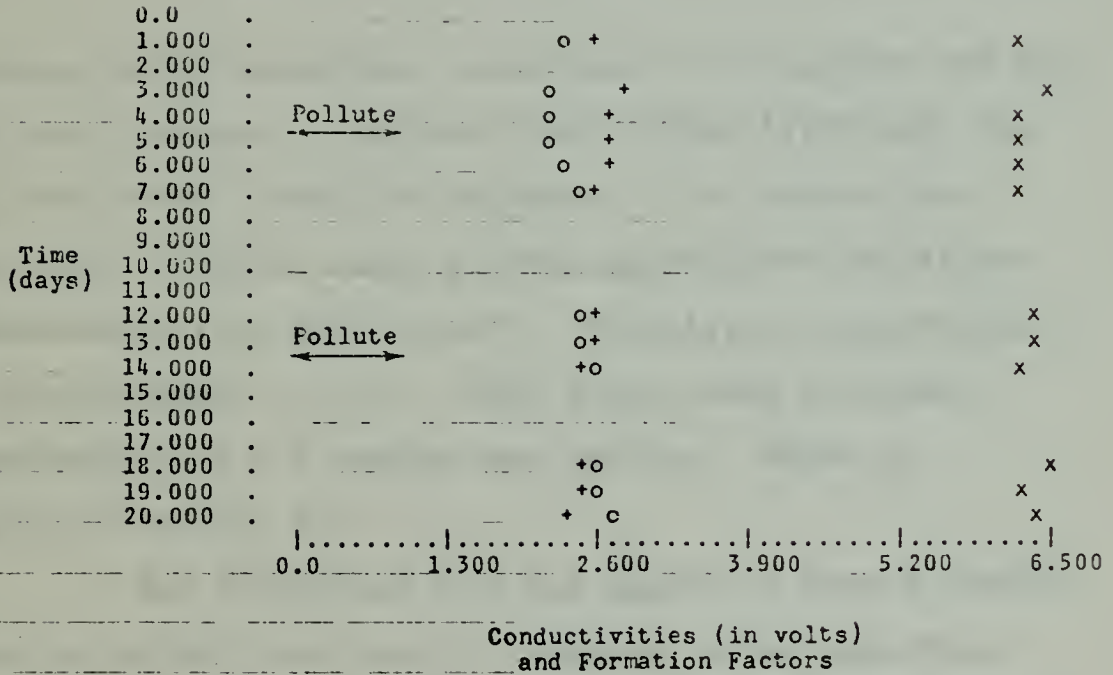


FIGURE 19. Dextrose in Illite (porosity - 65.4%)

4. A nitrogen fertilizer was the next pollutant to be studied. This particular pollutant was a solution mixed from "Ortho, Ortho-Gro Liquid Plant Food". Its composition was:

TABLE 6. Fertilizer Composition

Total N	12%
Phosphoric acid	6%
Soluble potash	6%
Iron	0.5%
Zinc	0.1%

Following label directions a solution of fertilizer and tap water was prepared. This was then diluted 1:100 into the free "sea water" above the sediments. The author felt that such a dilution might grossly approximate fertilizer concentration from farm run-off. Fertilizer concentration was approximately 30 ppm. After eight days, pollutant concentration in all samples was doubled. Refer to Figures 20 through 23.

The fertilizer does not appear to have a drastic effect on either sand sample. However, after pollution concentrations were increased to 60 ppm, both sands had higher water and soil conductivities.

In both clays, the fertilizer decreased, first the water conductivities and then the soil conductivities.

Reductions in the clay samples were approximately equal in magnitude to increases throughout the sands.

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.50	1.30	4.17
5	5.55	1.42	3.92
6	5.44	1.21	4.43
7	5.48	1.32	4.15
8	5.50	1.35	4.09
9	5.40	1.36	3.97
11	5.40	1.30	4.15
13	5.45	1.31	4.15
14	5.52	1.39	3.97
15	5.47	1.41	3.88
16	5.44	1.41	3.86

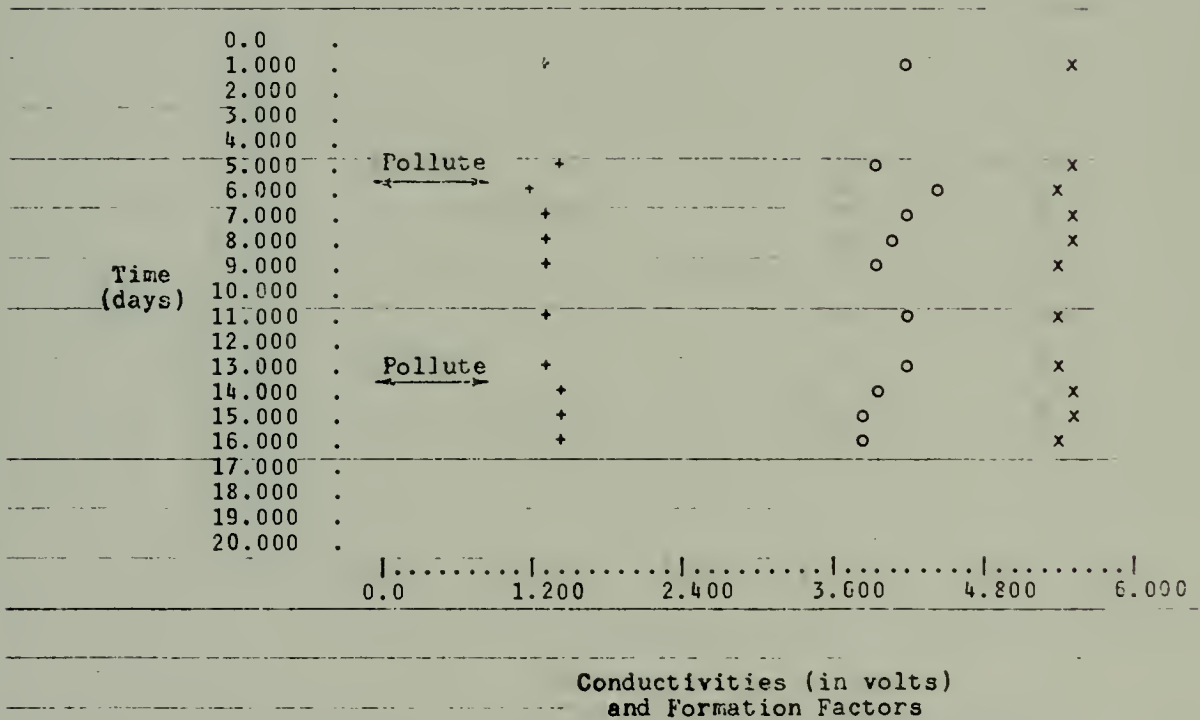


FIGURE 20. Fertilizer in Ottawa Sand (porosity - 35.9%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.50	1.48	3.72
5	5.55	1.48	3.72
6	5.37	1.38	3.89
7	5.40	1.39	3.88
8	5.49	1.43	3.85
9	5.38	1.42	3.79
11	5.39	1.39	3.88
13	5.42	1.42	3.82
14	5.50	1.51	3.64
15	5.43	1.50	3.64
16	5.42	1.40	3.87

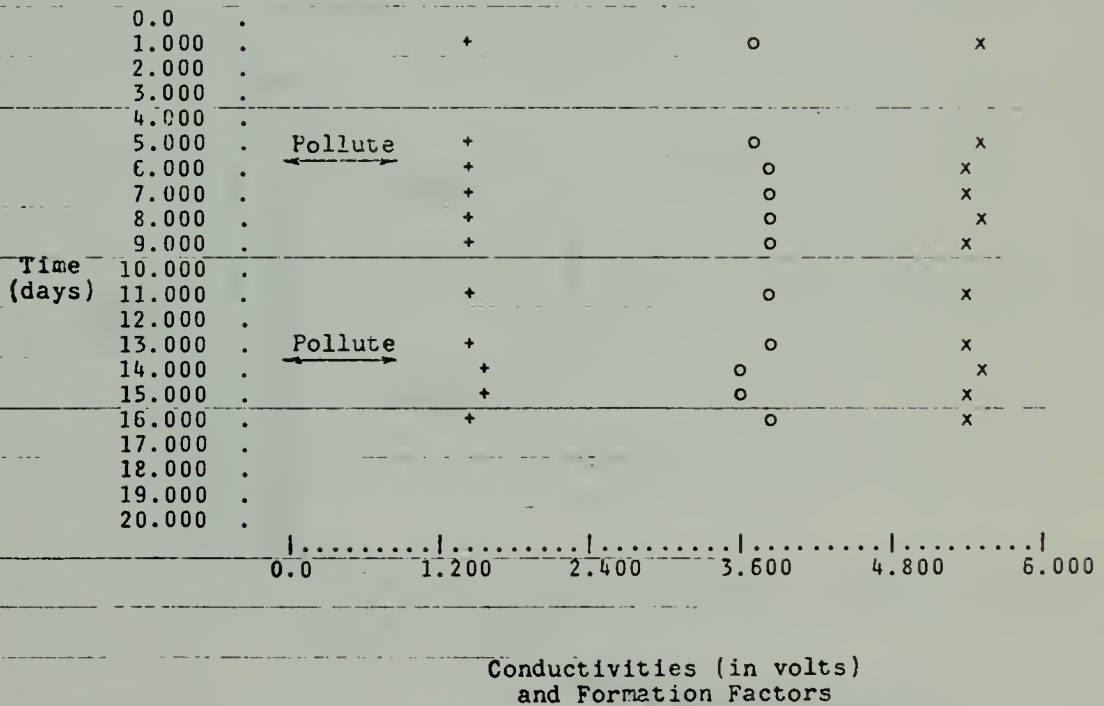


FIGURE 21. Fertilizer in Ottawa Sand (porosity - 41.0%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.04	3.83	1.58
5	6.08	3.99	1.52
6	5.78	3.80	1.52
7	5.79	3.76	1.54
8	5.82	3.79	1.54
9	5.83	3.66	1.59
11	5.85	3.62	1.62
13	5.98	3.66	1.63
14	5.89	3.70	1.59
15	5.87	3.77	1.56
16	5.85	3.60	1.63

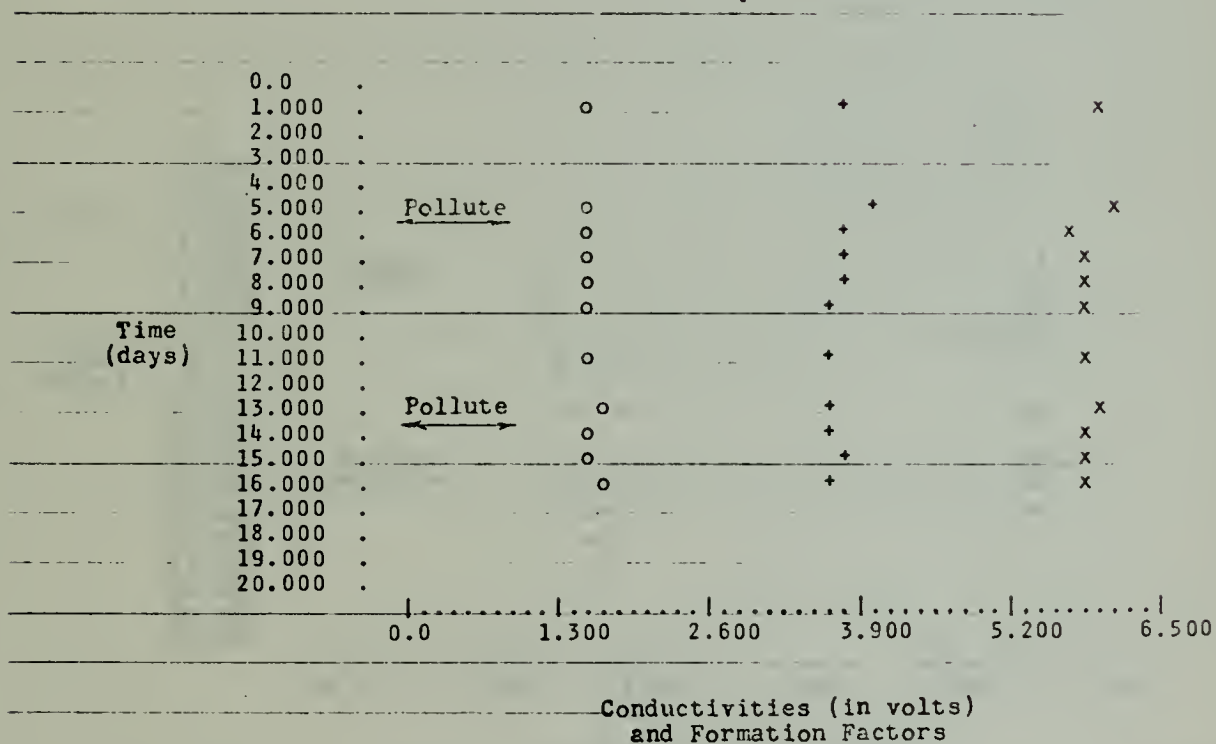


FIGURE 22. Fertilizer in Sodium Montmorillonite
(porosity - 85.6%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.98	3.01	2.32
5	7.07	3.36	2.10
6	6.87	3.23	2.13
7	6.87	3.17	2.17
8	6.84	2.99	2.29
9	6.82	2.96	2.30
11	6.83	2.87	2.38
13	6.83	2.80	2.44
14	6.83	2.84	2.40
15	6.83	2.70	2.53
16	6.88	2.70	2.55

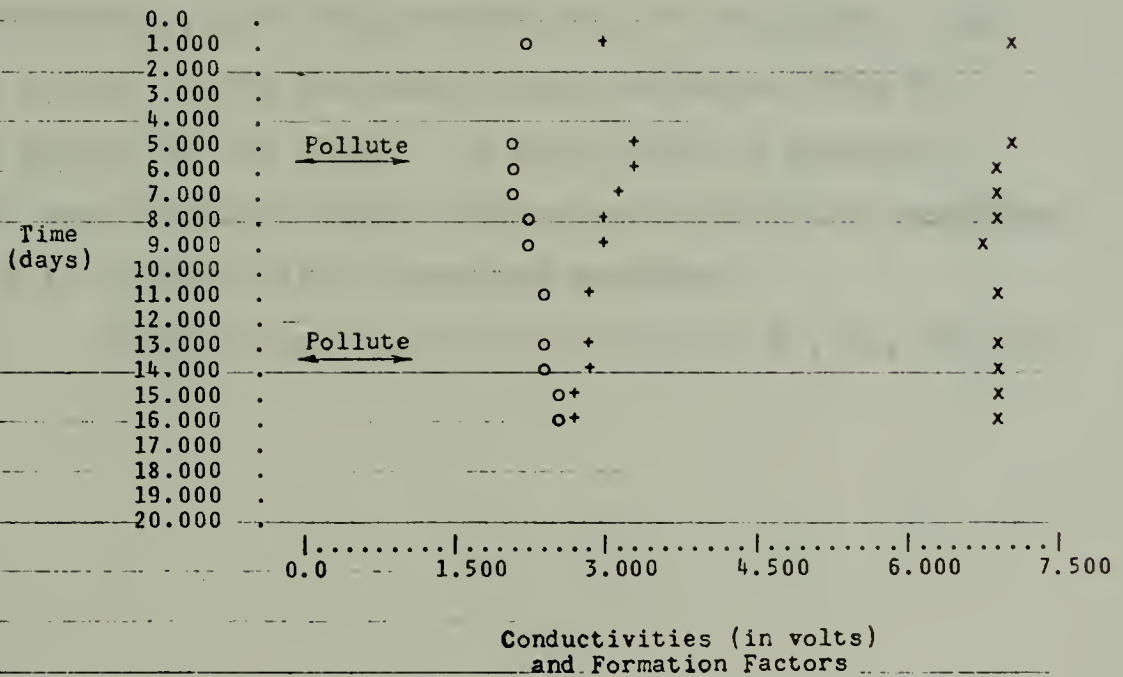


FIGURE 23. Fertilizer in Illite (porosity - 68.1%)

5. "Ortho Sevin Garden Dust", was pollutant five.

This substance is a more or less common pesticide used on individual plants. It can also be used to remove pests from small animals such as cats and dogs. It is 5% by weight carbaryl (1-naphthyl N-methylcarbamate) and 95% inert ingredients. Initial concentration above the sediments was 30 ppm. This dosage was repeated after eight days.

Definite decreases in water conductivities are noted for the sand samples, and also initially for both clays. Approximately mid-way through the test period, the clay water conductivities returned to initial values. Coincidentally, clay soil conductivities decreased. The trend points to the pesticide being withdrawn from the water column by the clays. No such trend is apparent on the sand readings. While water conductivities decreased, sand soil conductivities remained constant.

Results are contained in Figures 24, 25, 26 and

27.

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.50	1.40	3.92
2	5.50	1.33	4.12
3	5.51	1.32	4.18
4	5.36	1.31	4.09
5	5.34	1.27	4.21
7	5.42	1.24	4.37
9	5.40	1.29	4.19
10	5.47	1.40	3.91
11	5.51	1.35	4.08
12	5.42	1.30	4.17
15	5.44	1.34	4.06
16	5.46	1.37	3.99

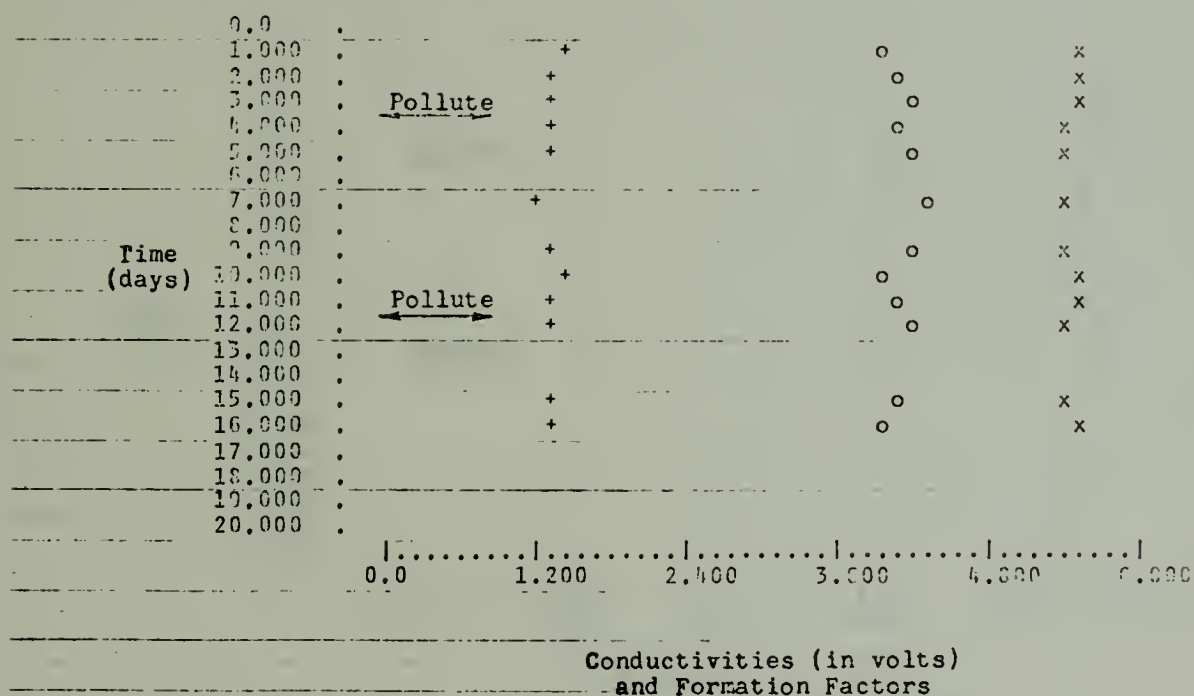
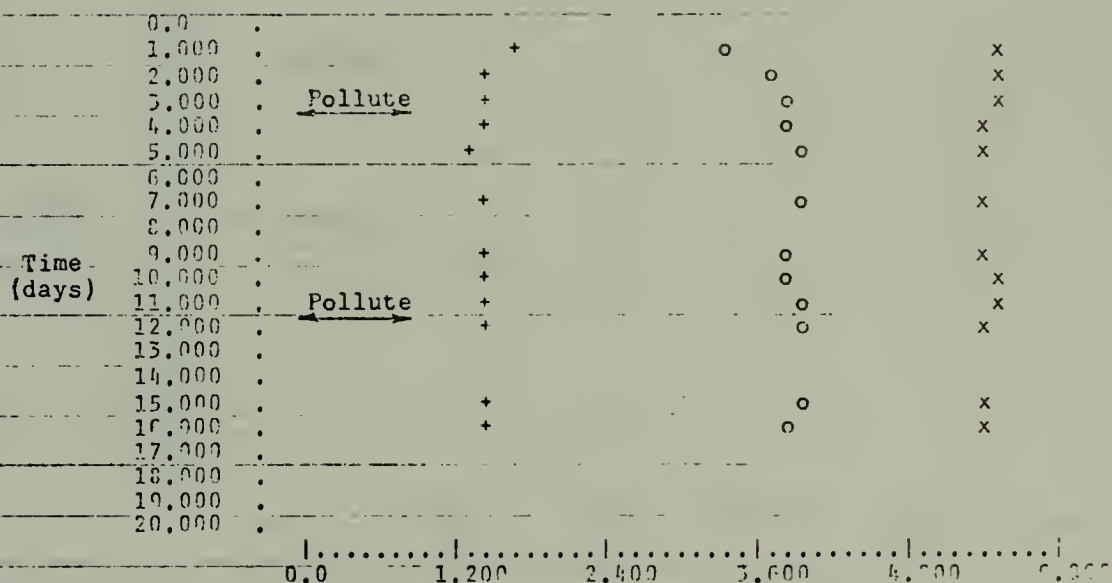


FIGURE 24. Pesticide in Ottawa Sand (porosity - 36.3%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.52	1.65	3.35
2	5.50	1.47	3.74
3	5.48	1.41	3.87
4	5.39	1.42	3.80
5	5.35	1.35	3.96
7	5.42	1.39	3.90
9	5.39	1.39	3.88
10	5.47	1.42	3.85
11	5.50	1.40	3.93
12	5.41	1.38	3.92
15	5.45	1.39	3.92
16	5.45	1.40	3.89



Conductivities (in volts)
and Formation Factors

FIGURE 25. Pesticide in Ottawa Sand (porosity - 42.2%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.96	3.99	1.49
2	5.80	3.90	1.49
3	5.84	3.85	1.52
4	5.75	3.83	1.50
5	5.75	3.72	1.55
7	5.80	3.78	1.53
9	5.73	3.67	1.56
10	5.92	3.72	1.59
11	5.98	3.68	1.63
12	5.84	3.71	1.57
15	5.98	3.75	1.59
16	5.89	3.71	1.59

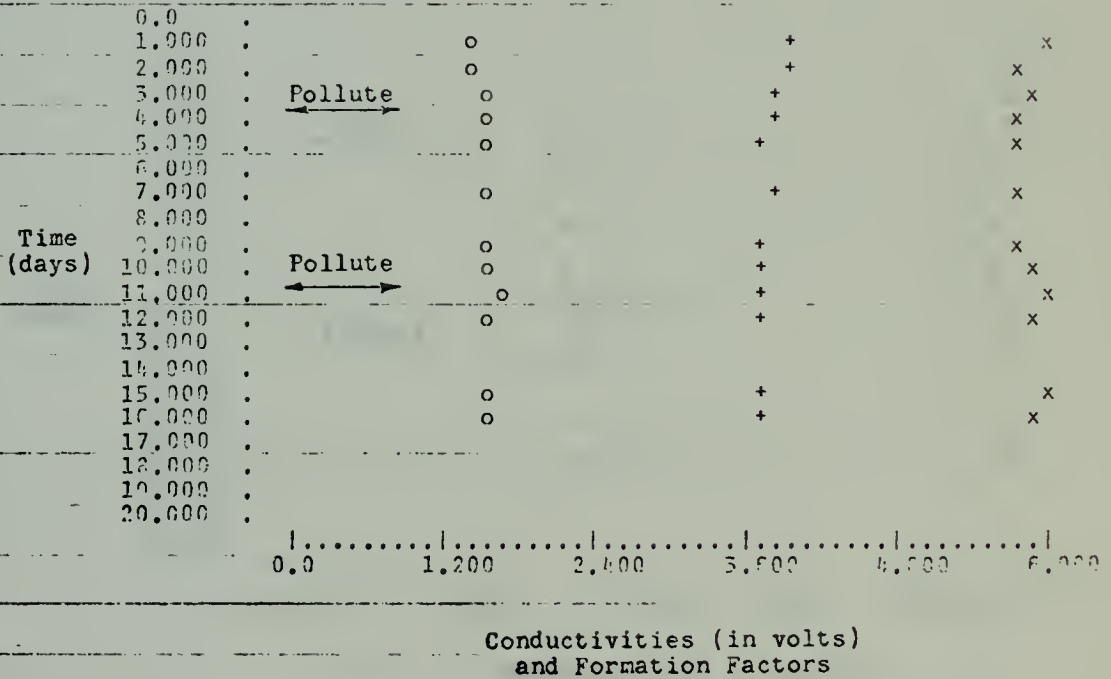


FIGURE 26. Pesticide in Sodium Montmorillonite
(porosity - 87.5%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.54	2.89	2.26
2	6.43	3.02	2.13
3	6.37	2.96	2.15
4	6.36	2.82	2.26
5	6.33	2.72	2.33
7	6.35	2.66	2.39
9	6.27	2.70	2.32
10	6.43	2.61	2.46
11	6.46	2.62	2.47
12	6.37	2.62	2.43
15	6.49	2.58	2.52
16	6.50	2.50	2.60

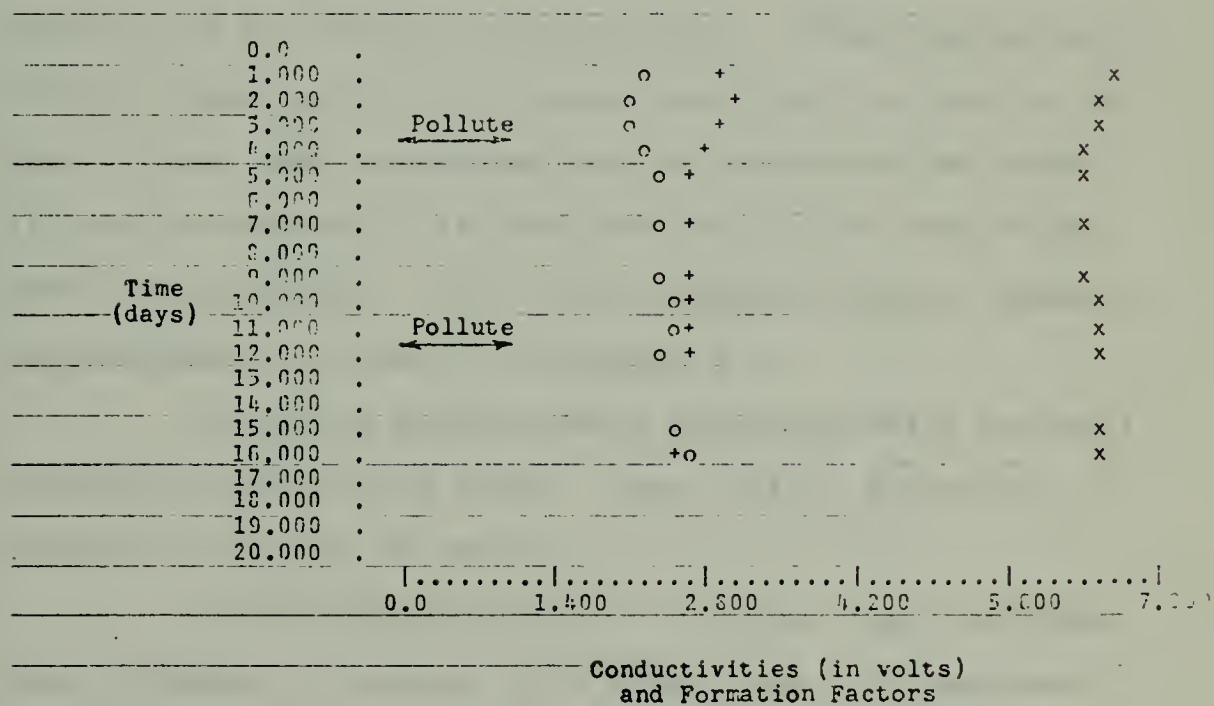


FIGURE 27. Pesticide in Illite (porosity - 65.6%)

6. Iron, the second heavy metal to be studied, was the next pollutant.

Iron sulfate was mixed with distilled water and then diluted into the samples. A 10 ppm concentration of iron was doubled to 20 ppm after ten days.

An interesting phenomena accompanied this particular pollutant. Within several hours after polluting with the first dose of iron, all the free water solutions turned yellow. By the time of the first set of readings, one day later, a yellow powder covered the soil surface of all samples. The iron had oxidized. This condition remained on all samples except illite. After approximately thirteen days, the illite showed absolutely no sign of the iron. Also, when the second dose of pollutant was added, all samples except illite had the yellow tint and "rust" particles amplified. The illite remained normal. Results are displayed in Figures 28 through 31.

The iron quite clearly increased water and soil conductivities in both sands. Very similar trends are evident in Figures 28 and 29.

The conductivities of the water over the clays also increased. However, both clays show a 7% decrease in soil conductivities apparently caused by the iron.

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.50	1.40	3.93
3	5.49	1.43	3.84
4	5.47	1.39	3.94
5	5.48	1.42	3.86
6	5.49	1.41	3.89
9	5.50	1.37	4.02
10	5.57	1.39	4.01
11	5.50	1.42	3.87
12	5.51	1.40	3.94
13	5.50	1.41	3.90
15	5.64	1.48	3.81
17	5.60	1.51	3.71
18	5.60	1.53	3.66

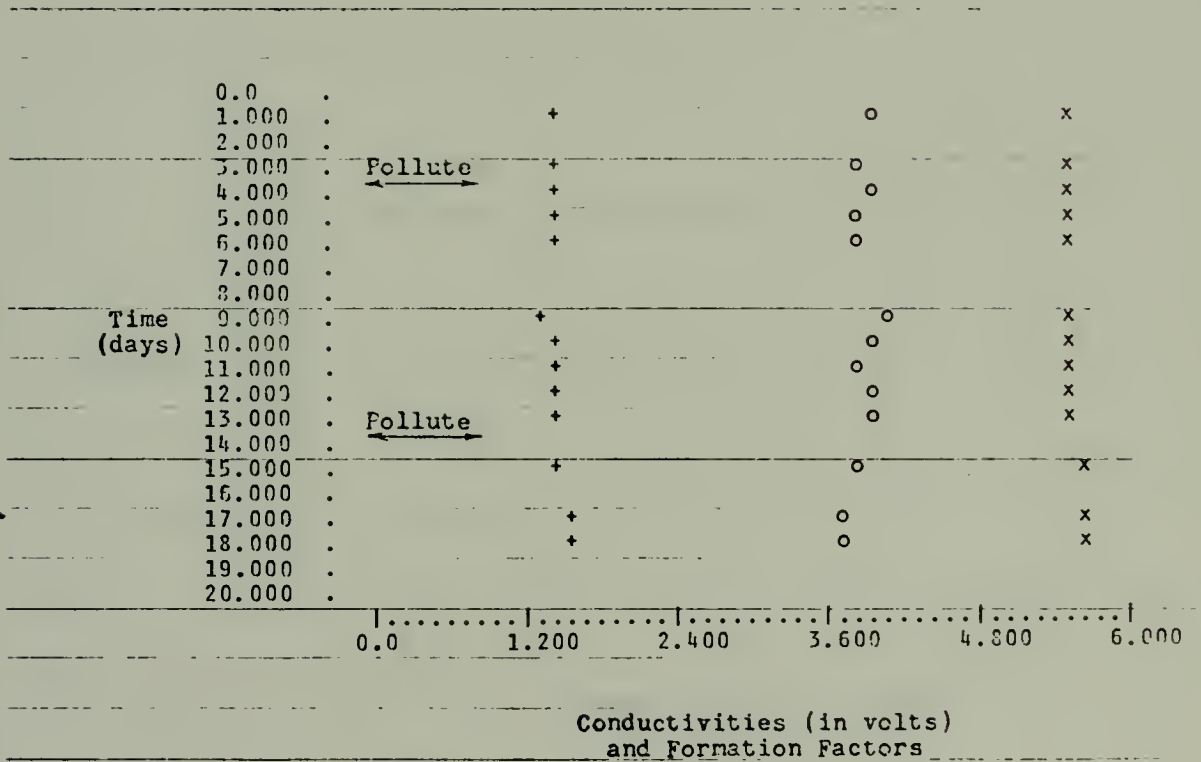


FIGURE 28. Iron in Ottawa Sand (porosity - 34.8%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.48	1.16	4.72
3	5.49	1.28	4.29
4	5.46	1.35	4.04
5	5.49	1.33	4.13
6	5.52	1.32	4.18
9	5.50	1.36	4.04
10	5.57	1.39	4.01
11	5.52	1.39	3.97
12	5.51	1.39	3.96
13	5.51	1.40	3.94
15	5.61	1.41	3.98
17	5.60	1.41	3.97
18	5.62	1.44	3.90

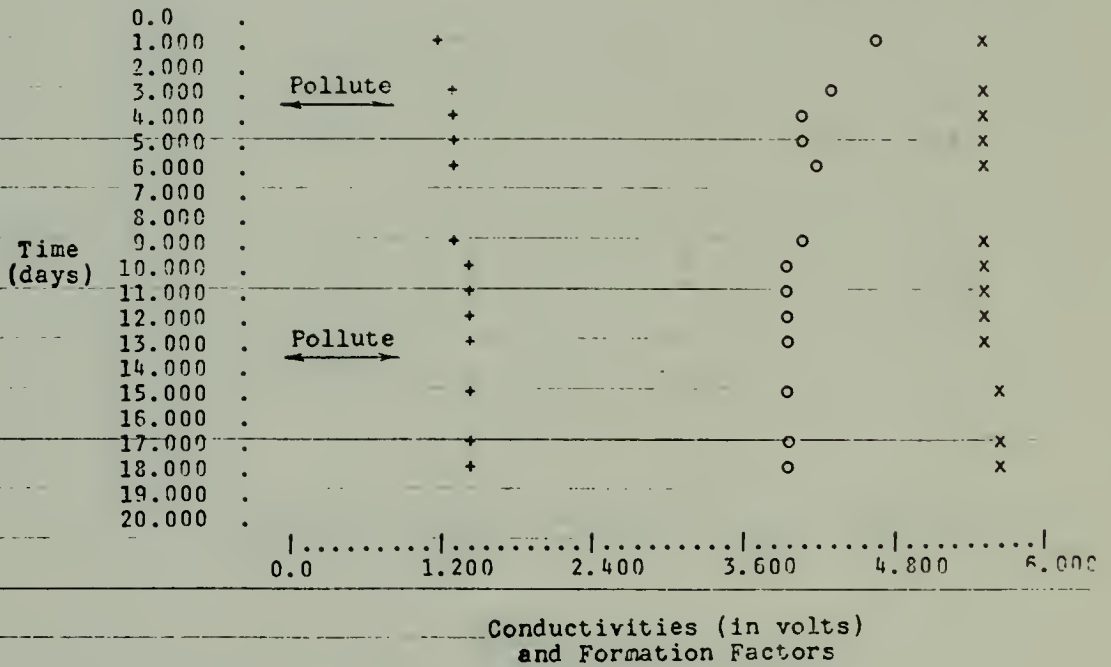


FIGURE 29. Iron in Ottawa Sand (porosity - 42.7%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.91	3.80	1.56
3	5.89	3.70	1.59
4	5.86	3.72	1.58
5	5.88	3.66	1.61
6	5.97	3.62	1.65
9	6.01	3.55	1.69
10	6.03	3.54	1.70
11	5.99	3.52	1.70
12	5.89	3.53	1.67
13	5.95	3.45	1.72
15	6.03	3.60	1.68
17	6.05	3.51	1.72
18	5.96	3.52	1.69

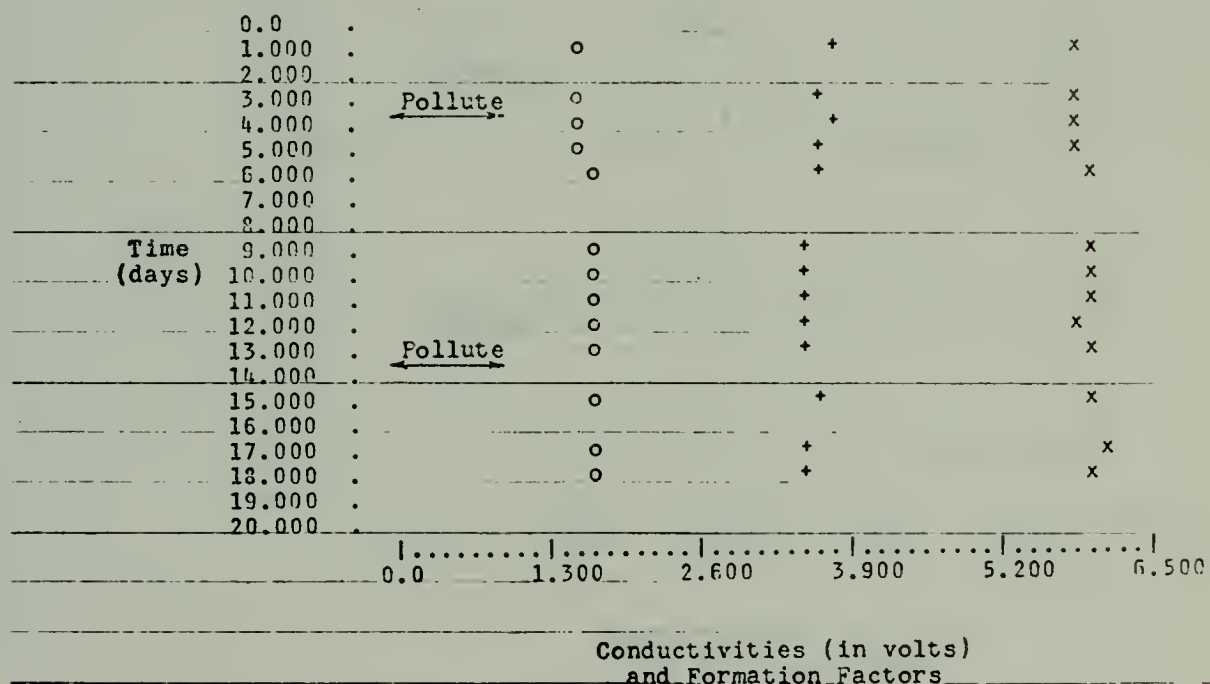
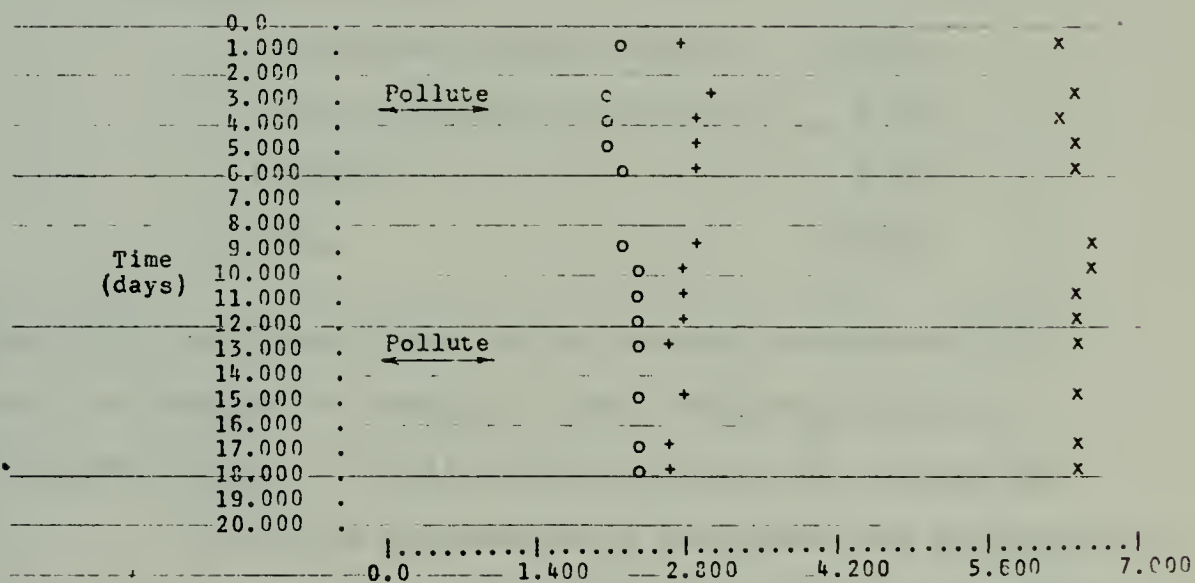


FIGURE 30. Iron in Sodium Montmorillonite (porosity - 86.1%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.35	2.83	2.24
3	6.41	3.04	2.11
4	6.29	2.99	2.10
5	6.37	2.96	2.15
6	6.42	2.88	2.23
9	6.52	2.92	2.23
10	6.51	2.78	2.34
11	6.46	2.75	2.35
12	6.44	2.78	2.32
13	6.47	2.71	2.39
15	6.47	2.78	2.33
17	6.40	2.63	2.43
18	6.43	2.64	2.44



Conductivities (in volts)
and Formation Factors

FIGURE 31. Iron in Illite (porosity - 67.8%)

7. Pollutant number seven was "Devoe Vinyl Acrylic Latex House Paint". Composition of the paint is listed in Table 7.

TABLE 7. Paint Composition

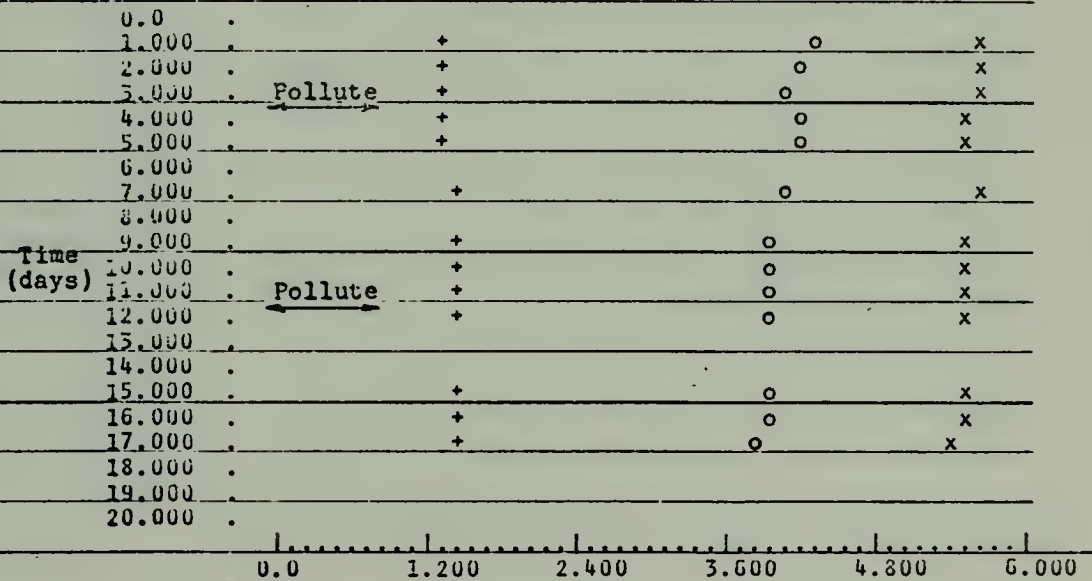
Pigment 31.6%	
Titanium dioxide	63.3%
Zinc oxide	13.9%
Ca Carbonate	17.1%
Silica	5.7%
Vehicle 68.4%	
PV acetate-acrylic resin	27.0%
Tall oil-Linseed-Alkyd resin	2.2%
Alcohol	5.0%
Water	65.8%

The first pollutant dose yielded a paint concentration over the samples of nearly 17 ppm. This was doubled eight days later. Results are in Figures 32 through 35.

The paint substantially decreased the conductivity of all free water. An approximate 2% decrease in readings is apparent.

In the soil readings, both clays also showed substantial conductivity decreases. The sands, on the other hand, remained relatively constant. The results seem to indicate a certain affinity between the clay particles and the paint.

Time (days)	Conductivity		Formation Factor (c)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.61	1.30	4.32
2	5.60	1.35	4.15
3	5.62	1.37	4.10
4	5.52	1.32	4.18
5	5.55	1.31	4.24
7	5.60	1.38	4.05
9	5.49	1.39	3.95
10	5.52	1.38	4.00
11	5.52	1.40	3.94
12	5.54	1.42	3.90
15	5.53	1.41	3.92
16	5.56	1.41	3.94
17	5.45	1.41	3.87



Conductivities (in volts)
and Formation Factors

FIGURE 32. Latex Paint in Ottawa Sand (porosity - 32.9%)

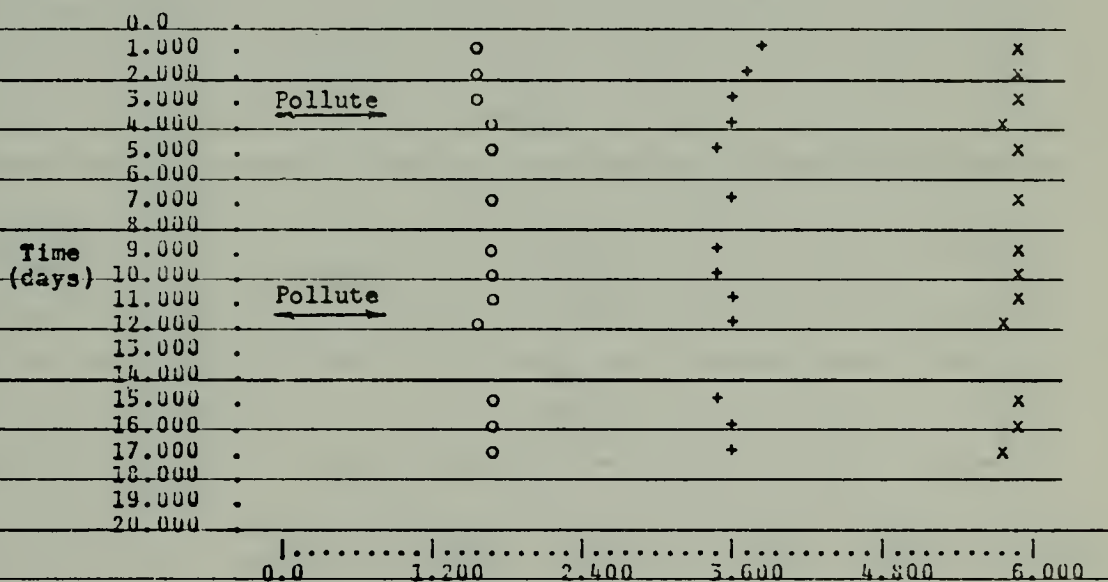
Time (days)	Conductivity		Formation Factor (n)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.50	1.43	3.85
2	5.50	1.43	3.65
3	5.49	1.40	3.92
4	5.35	1.37	3.91
5	5.39	1.41	3.82
7	5.42	1.40	3.87
9	5.38	1.43	3.76
10	5.41	1.43	3.78
11	5.40	1.40	3.86
12	5.38	1.45	3.71
15	5.39	1.45	3.67
16	5.43	1.43	3.80
17	5.35	1.41	3.79

0.0	.				
1.000	.	+	o		x
2.000	.	+	o		x
3.000	.	<u>Pollute</u> +	o		x
4.000	.	+	o		x
5.000	.	+	o		x
6.000	.				
7.000	.	+	o		x
8.000	.				
9.000	.	+	o		x
10.000	.	+	o		x
11.000	.	<u>Pollute</u> +	o		x
12.000	.	+	o		x
13.000	.				
14.000	.				
15.000	.	+	o		x
16.000	.	+	o		x
17.000	.	+	o		x
18.000	.				
19.000	.				
20.000	.				
.....					
0.0		1.100	2.200	3.300	4.400 5.500

Conductivities (in volts)
and Formation Factors

FIGURE 33. Latex Paint in Ottawa Sand (porosity - 40.9%)

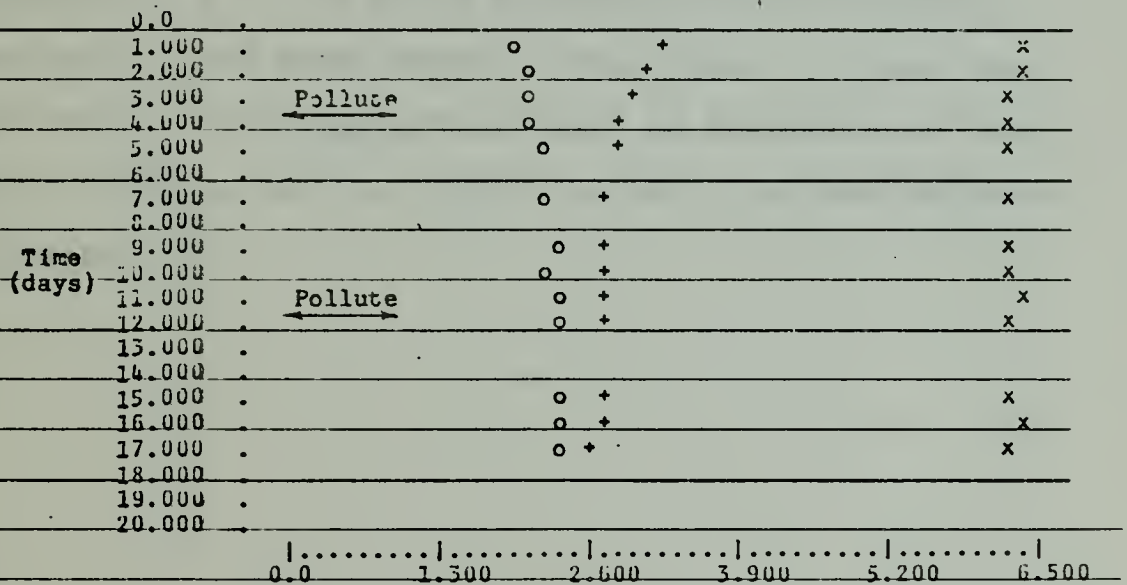
Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.90	3.84	1.54
2	5.92	3.73	1.59
3	5.87	3.64	1.61
4	5.81	3.58	1.62
5	5.83	3.49	1.67
7	5.93	3.57	1.66
9	5.82	3.50	1.66
10	5.83	3.53	1.65
11	5.87	3.62	1.62
12	5.76	3.58	1.61
15	5.87	3.47	1.69
16	5.88	3.55	1.66
17	5.81	3.58	1.62



Conductivities (in volts)
and Formation Factors

FIGURE 34. Latex Paint in Sodium Montmorillonite
(porosity - 85.4%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.35	3.22	1.97
2	6.34	3.10	2.05
3	6.28	3.03	2.07
4	6.20	2.92	2.12
5	6.22	2.81	2.21
7	6.29	2.79	2.25
9	6.26	2.74	2.29
10	6.27	2.76	2.27
11	6.32	2.76	2.29
12	6.25	2.68	2.33
15	6.20	2.70	2.30
16	6.32	2.68	2.36
17	6.22	2.61	2.38



Conductivities (in volts)
and Formation Factors

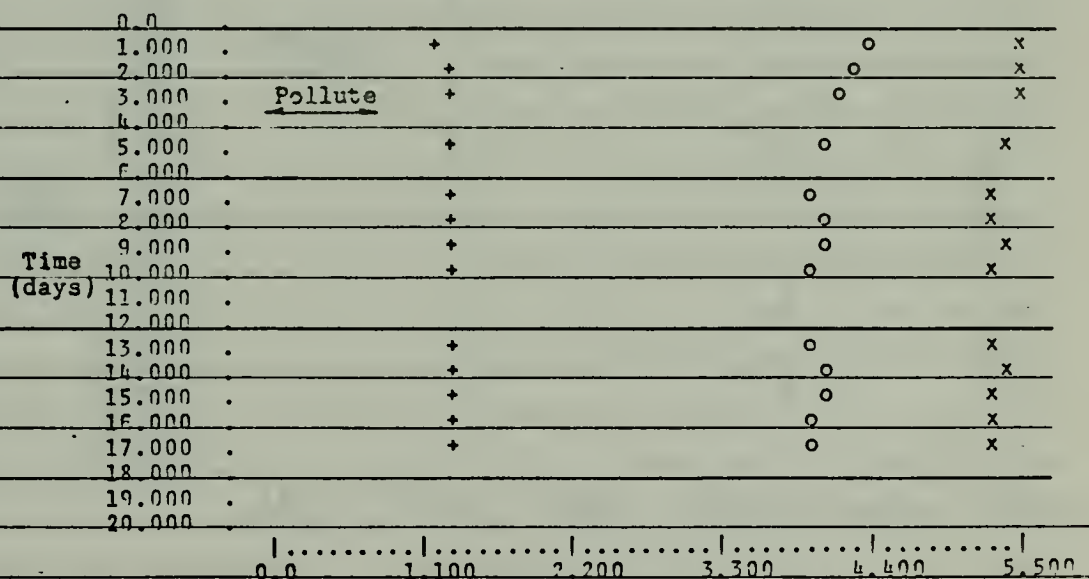
FIGURE 35. Latex Paint in Illite (porosity - 65.8%)

8. Isopropyl alcohol was selected to pollute the next four sediments. A slight change in procedure was instituted with this series. Rather than provide two low pollution doses, it was decided to inject one relatively large dose and then observe the results with time.

Ten ml of alcohol was added to the equivalent of one liter free "sea water" over each sample. The concentration was then 10 ppt alcohol. Figures 36 through 39 display the data and results.

Results are very similar to those just presented for the paint. All water conductivities, and the soil conductivities of the clays substantially and clearly decreased. Both sands showed little change in soil conductivities. This is most probably an indication of the clays' affinity for the alcohol molecule, as was mentioned in Chapter III.

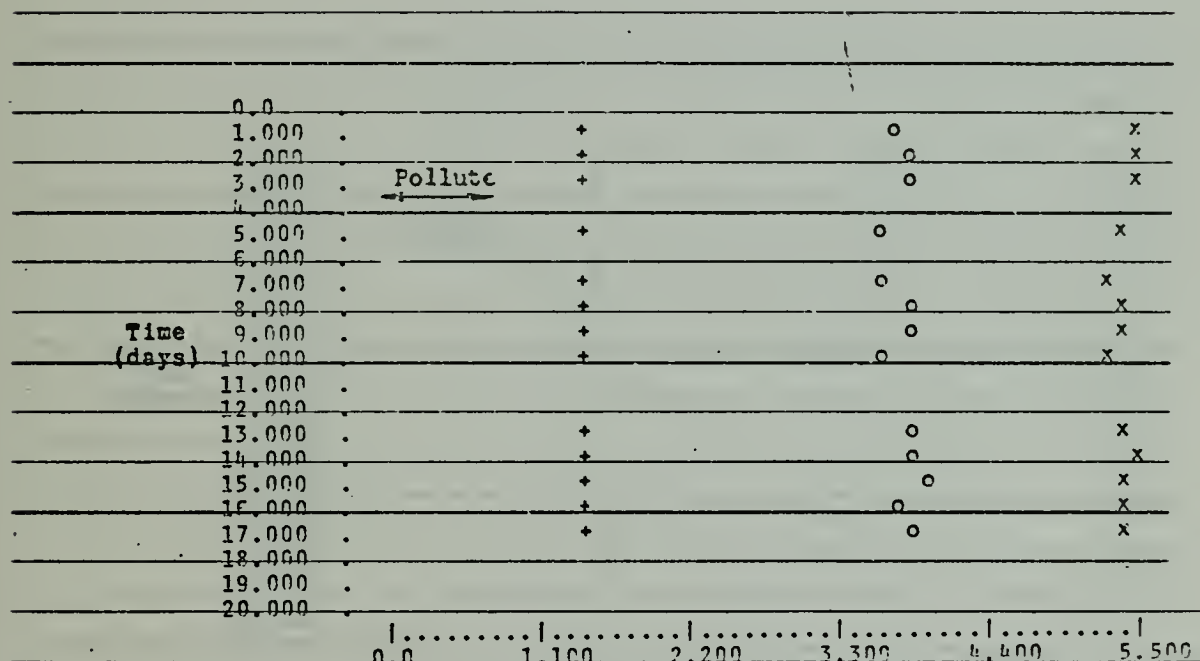
Time (days)	Conductivity		Formation Factor (c)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.49	1.25	4.39
2	5.49	1.27	4.32
3	5.48	1.32	4.15
5	5.37	1.33	4.04
7	5.32	1.35	3.94
8	5.29	1.30	4.07
9	5.34	1.32	4.05
10	5.24	1.32	3.97
13	5.30	1.33	3.99
14	5.37	1.31	4.10
15	5.32	1.31	4.03
16	5.30	1.33	3.99
17	5.31	1.34	3.96



Conductivities (in volts)
and Formation Factors

FIGURE 36. Alcohol in Ottawa Sand (porosity - 35.3%)

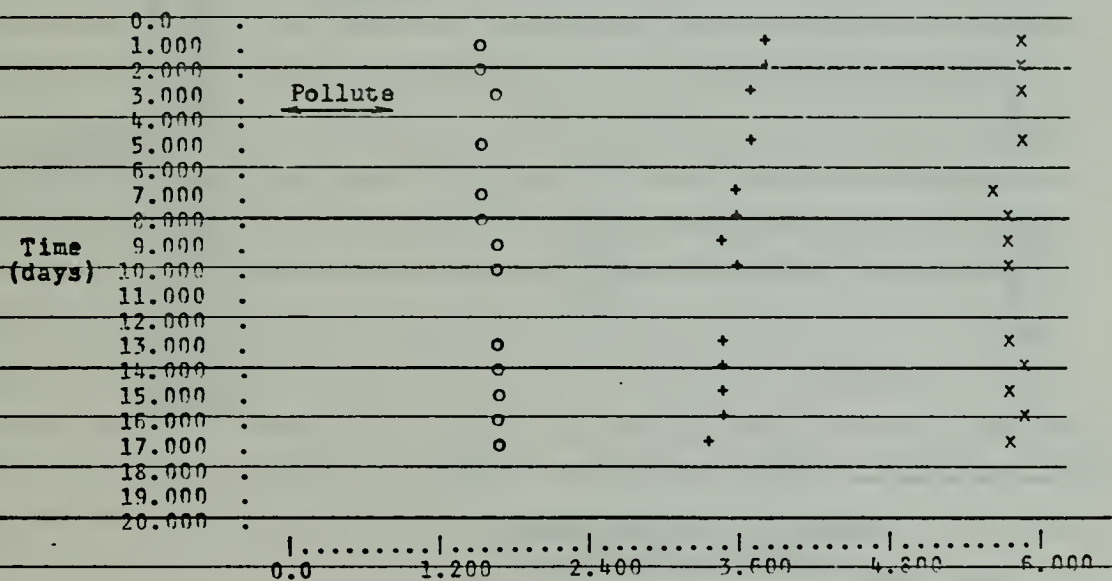
Time (days)	Conductivity		Formation Factor (c)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.50	1.45	3.79
2	5.49	1.42	3.87
3	5.50	1.44	3.62
5	5.40	1.48	3.65
7	5.28	1.45	3.64
8	5.37	1.41	3.81
9	5.39	1.42	3.80
10	5.32	1.45	3.64
13	5.38	1.41	3.82
14	5.46	1.42	3.85
15	5.41	1.38	3.92
16	5.35	1.43	3.74
17	5.35	1.40	3.82



Conductivities (in volts)
and Formation Factors

FIGURE 37. Alcohol in Ottawa Sand (porosity - 38.2%)

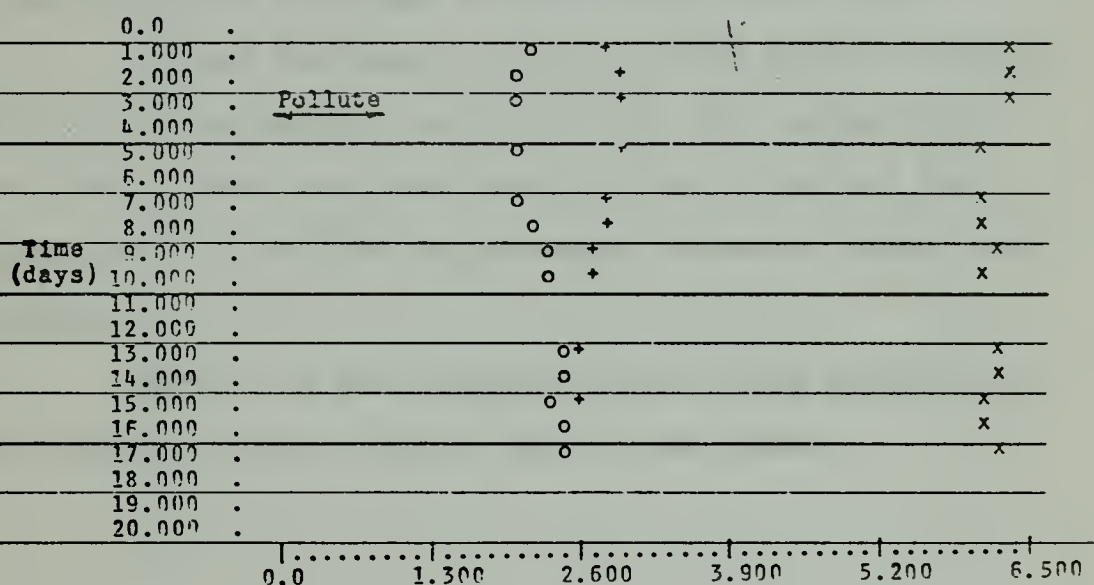
Time (days)	Conductivity		Formation Factor (c)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.90	3.79	1.56
2	5.92	3.79	1.56
3	5.93	3.66	1.62
5	5.84	3.68	1.59
7	5.66	3.57	1.59
8	5.75	3.57	1.63
9	5.73	3.50	1.64
10	5.73	3.54	1.62
13	5.73	3.45	1.60
14	5.90	3.45	1.71
15	5.80	3.45	1.68
16	5.85	3.50	1.67
17	5.73	3.38	1.70



Conductivities (in volts)
and Formation Factors

FIGURE 38. Alcohol in Sodium Montmorillonite
(porosity - 85.2%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (r)	Voltage of Soil (s)	
1	6.40	2.89	2.21
2	6.34	3.02	2.10
3	6.34	3.07	2.09
5	6.12	3.00	2.01
7	6.05	2.83	2.10
8	6.15	2.81	2.15
9	6.18	2.70	2.28
10	6.15	2.66	2.29
13	6.24	2.58	2.12
14	6.20	2.51	2.17
15	6.10	2.56	2.38
16	6.16	2.49	2.17
17	6.19	2.57	2.48



Conductivities (in volts)
and Formation Factors

FIGURE 39. Alcohol in Illite (porosity - 65.7%)

9. The final pollutant chosen to study was #6 fuel oil. As with the isopropyl alcohol only one large dose of pollutant was used. Ten ml of fuel oil was poured on the surface of the water of each sample. Pollution concentration was 10 ppt.

The data as presented in Figures 40 through 43 show far fewer data points than earlier work. This was due to the difficulty in handling the fuel oil. Extreme care had to be exercised to assure that the probe would not become covered with the soil. The author, therefore, decided to reduce readings to once every other day.

In all instances, the oil first reduced the conductivity of the water, then decreased the conductivity of the soil. The relative insolubility of the oil was demonstrated by the time lag between the water effect and soil effect.

Again, as has been seen with other samples, the clays exhibit larger effects than do the sands.

Time (days)	Conductivity		Formation Factor (c)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.56	1.30	4.28
4	5.55	1.29	4.30
5	5.54	1.28	4.33
6	5.55	1.32	4.20
8	5.51	1.33	4.14
11	5.49	1.36	4.04
13	5.55	1.36	4.08
15	5.45	1.39	3.92
17	5.33	1.30	4.10

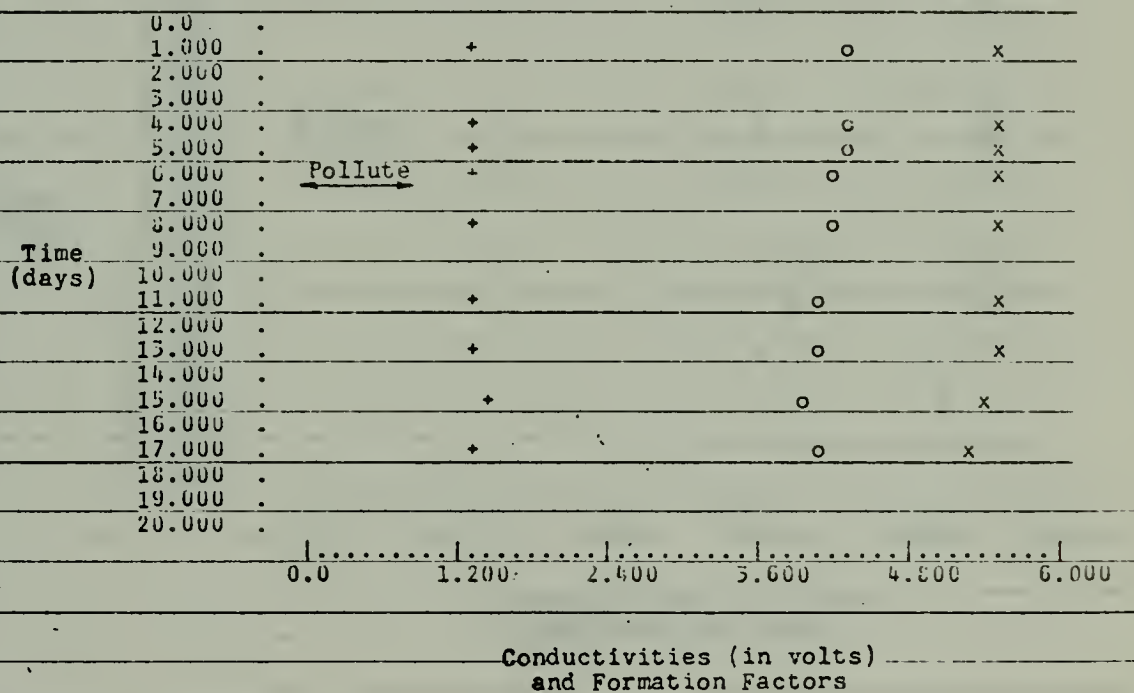


FIGURE 40. Oil in Ottawa Sand (porosity - 34.8%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	5.54	1.52	3.65
4	5.51	1.52	3.60
5	5.54	1.50	3.69
6	5.54	1.51	3.67
8	5.43	1.50	3.62
11	5.50	1.39	3.96
13	5.54	1.39	3.99
15	5.51	1.44	3.69
17	5.21	1.38	3.78

	0.0	.			
	1.000	.	+	o	x
	2.000	.			
	3.000	.			
	4.000	.	+	o	x
	5.000	.	+	o	x
	6.000	.	+	o	x
	7.000	.			
	8.000	.	+	o	x
	9.000	.			
Time (days)	10.000	.			
	11.000	.	+	o	x
	12.000	.			
	13.000	.	+	o	x
	14.000	.			
	15.000	.	+	o	x
	16.000	.			
	17.000	.	+	o	x
	18.000	.			
	19.000	.			
	20.000	.			

0.0 1.200 2.400 3.600 4.800 6.000

Conductivities (in volts)
and Formation Factors

FIGURE 41. Oil in Ottawa Sand (porosity - 40.0%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.14	3.88	1.58
4	5.90	3.82	1.54
5	6.08	3.76	1.62
6	6.02	3.72	1.62
8	5.99	3.65	1.64
11	5.93	3.55	1.67
13	5.79	3.51	1.65
15	5.51	3.39	1.63
17	5.50	3.30	1.67

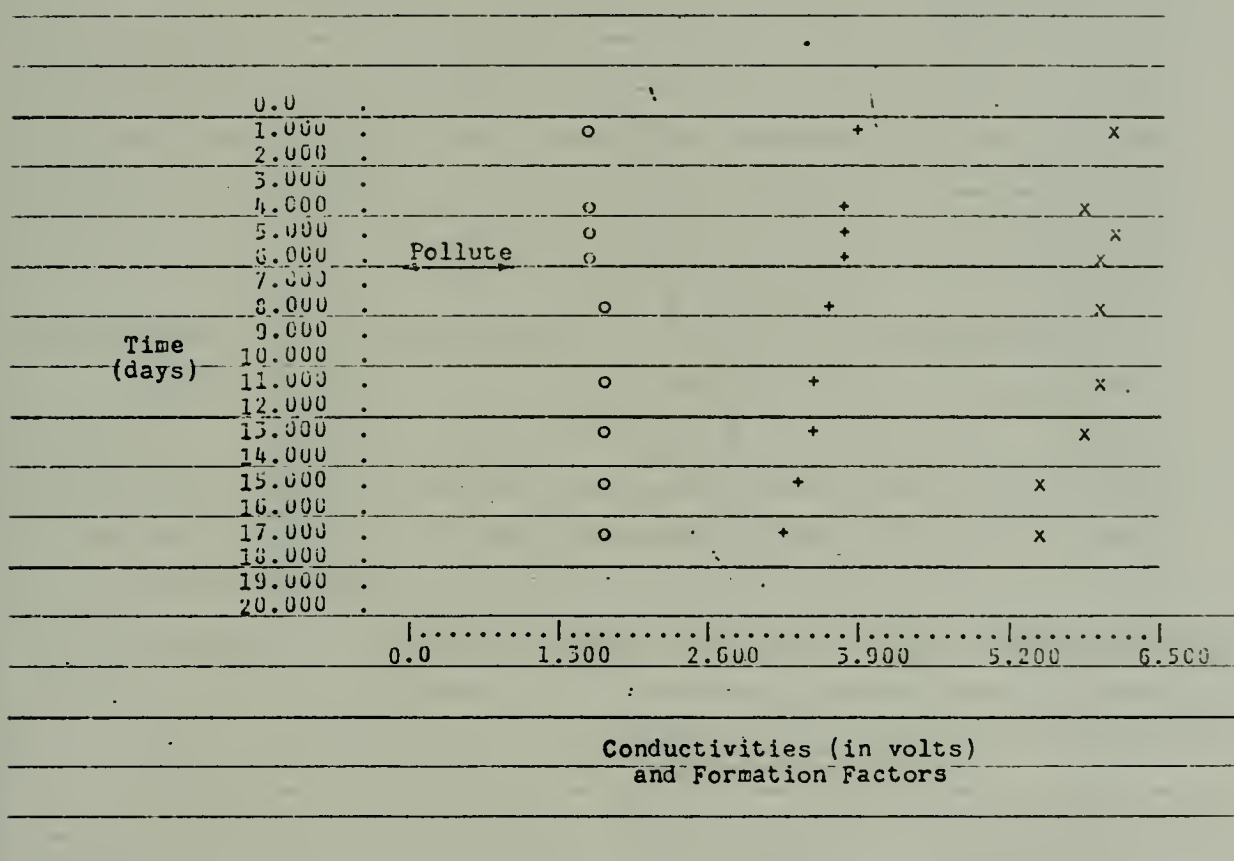
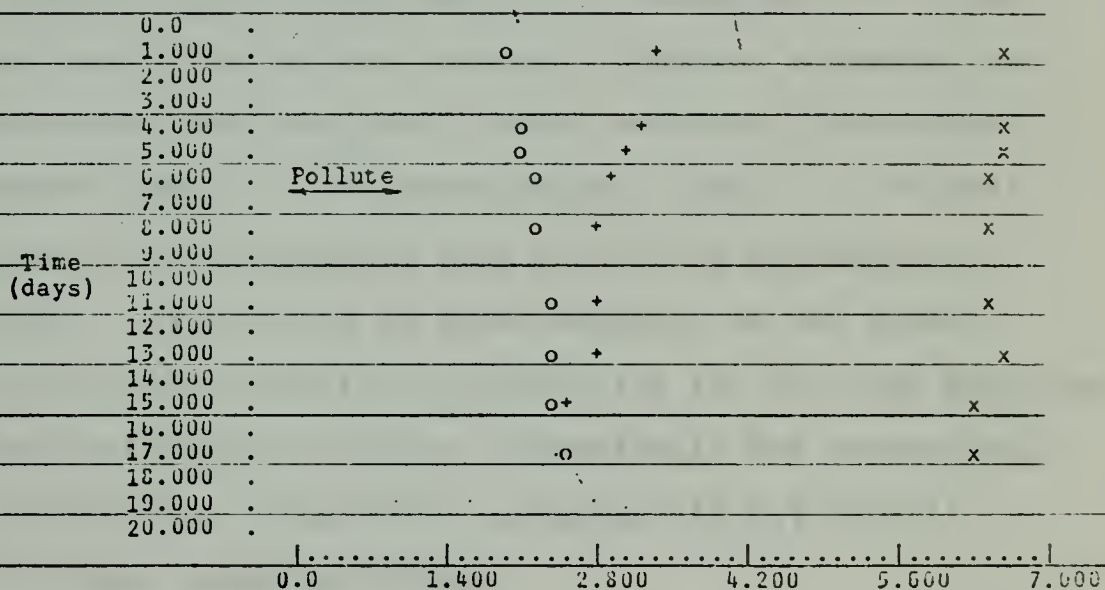


FIGURE 42. Oil in Sodium Montmorillonite (porosity - 85.8%)

Time (days)	Conductivity		Formation Factor (o)
	Voltage of Water (x)	Voltage of Soil (+)	
1	6.55	3.29	1.99
4	6.51	3.16	2.06
5	6.55	3.06	2.14
6	6.50	2.98	2.18
8	6.46	2.87	2.25
11	6.50	2.77	2.35
13	6.51	2.75	2.37
15	6.28	2.57	2.44
17	6.30	2.56	2.46



Conductivities (in volts)
and Formation Factors

FIGURE 43. Oil in Illite (porosity - 65.8%)

Interpretation

After performing the pollution tests, the author feels that several items of interest should be discussed.

First is the opinion of the author that pollution in a marine sediment can be detected through electrical conductivity methods. Some pollutants are considerably easier to identify than others, and concentrations and soil types certainly have an effect. Yet detection in clean soil was generally possible.

In polluting the soils and taking the readings, the author noted an additional clay characteristic which undoubtedly affected the results. Whenever a reading was taken on the clay samples, a small amount of clay would resuspend itself in the water column. Prior to the next reading, this resuspended clay would have settled out of solution. In so doing it seems apparent to the author that this was an excellent opportunity for the clay particles to trap pollution molecules, electrically and mechanically. The heavier and larger sand particles did not exhibit any of these characteristics.

Finally, a word concerning the pollution results on illite. On a case-by-case basis, the illites would appear to have reacted most dramatically to a pollutant. However, when all the results are reviewed a disturbing trend is evidenced. Virtually all the illite samples experienced a decrease in soil conductivities during the tests. The author can assure any readers that sediment

volumes (and thus the sediment porosities) were closely monitored throughout the testing and did not change once they had stabilized after sedimentation. Yet it does not appear totally logical that when sodium montmorillonite is behaving in one way toward a pollutant, illite should behave oppositely. The only explanation this author can provide at this time, involves the illite structure. Possibly small structural changes on the particle level were occurring to the illite with time. In so doing, perhaps the tortuosity was increased (without noticeably altering the porosity) and thereby the soil conductivity decreased.

This one confusing aspect should not diminish the overall success of the tests. Various pollutants have been detected in artificial marine sediments.

V. FIELD TESTING

To further verify the use of the microlaterolog as a pollution indicator, a limited survey of the Quonset Point area was proposed. In 1972, Baird and Killoy (24) performed a pollution analysis for the Navy immediately south of Quonset Point Naval Air Station. During the analysis, Killoy also obtained conductivity readings of the area using a microlaterolog. There therefore existed a relatively in-depth soil and pollution analysis (comprised of grain size distribution, organic content, hydrocarbon content, and heavy metal concentration) which had been correlated to area formation factors. Considerable pollution was discovered over virtually the entire area which was attributed to various Navy operations.

This author felt that since the Baird and Killoy report, a natural change throughout the area was likely. This appeared logical since all Navy operations had ceased between June, 1972 and May, 1973 (25). If the pollutant levels of the area had changed, then a conductivity survey should yield a corresponding change in formation factors.

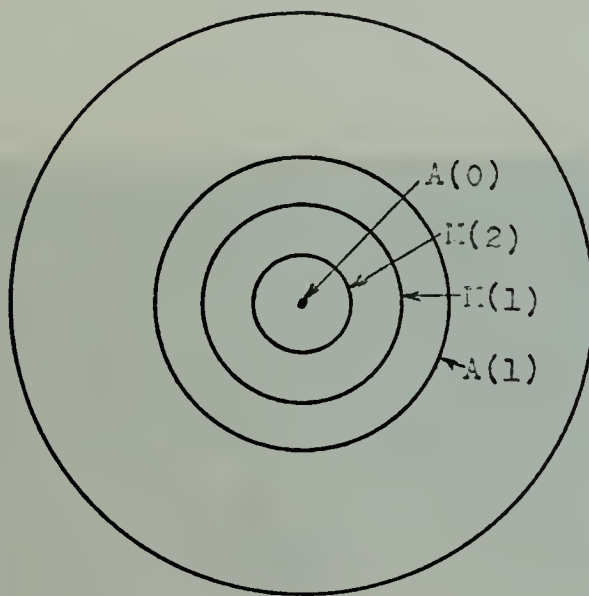
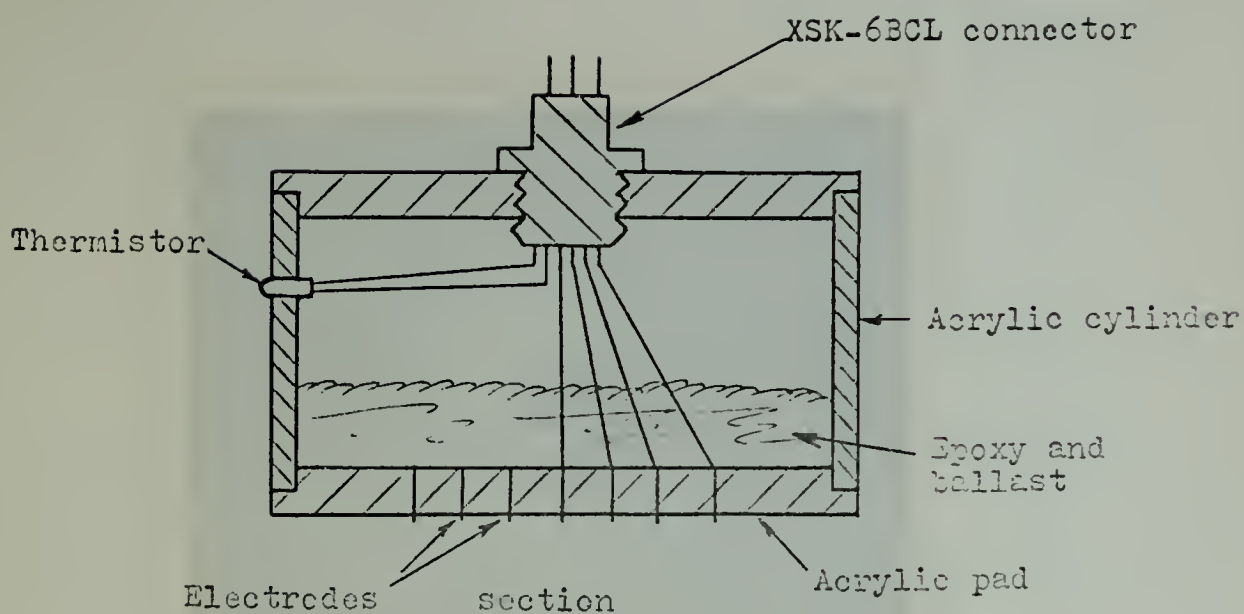
Equipment

An attempt was made to locate the field microlaterolog that Killoy had used. When properly calibrated, that probe would have insured a good correlation to the earlier data. However, the Killoy device could not be

located. A large, field microlaterolog was then constructed following all critical parameters from the Killoy system.

The field probe was a short cylinder with the four electrodes on one end of the cylinder, thermistor through the side, and connection plug on the opposite end (see Figures 44 and 45). The cylinder itself was six inches outside diameter, 3.5 inches tall, and had walls 0.25 inches thick, made of acrylic plastic. The ends were 0.50-inch thick acrylic sheet, turned to six inches in diameter. On the bottom, three grooves were turned into the face. These were one, two, and three inches in diameter. A center point was also drilled. This work provided the layout for the four electrodes necessary for the microlaterolog. A thermistor, identical to that used on the laboratory pad, was placed through the cylinder wall. In the top face, a hole was drilled and tapped for a Marsh and Marine XSK-6BCL connector. The connector provided six pins for internal connection to the four electrodes and two thermistor leads. Electrodes were formed from Kynar wire, exactly as was used in the laboratory. The electrodes and thermistor were potted into place with marine epoxy. In addition to providing an excellent bond between the wires and the acrylic, the epoxy served to make the wiring holes watertight.

The ends of the cylinder were cemented in place using acrylic solvent. Prior to cementing the top plate,



Plan

scale 1" = 2"

FIGURE 44. Field Microlaterolog



FIGURE 45. Field Microlaterolog

the inside of the probe was filled with nearly five pounds of lead shot and sufficient epoxy to hold the shot in place. The shot acted as ballast. Submerged weight of the probe was approximately three pounds. This provides a pressure on the soil of approximately 0.1 psi. The three major probe parameters (electrode size, thermistor, and probe pressure on soil) agree exactly with the Killoy system.

A Marsh and Marine type RMS-6SFS connector was connected to a reel of Belden 8467-18AWG jacketed cable. This provided the connection from the pad to the instrumentation. The instrumentation (signal conditioner and volt meter) was as used in the laboratory.

Any small AC power source is sufficient to drive the instrumentation. For this study, a 12-volt airplane battery and AC-DC inverter were used. However, a small AC generator would have worked equally well.

Testing Procedure

The following description of the study area comes from Killoy (15):

"The study area is in Narragansett Bay, Rhode Island, immediately south of Quonset Point. The bottom topography is dominated by a shallow depression within the 12-foot contour line. A large area of the shore is covered by concrete runways and for about half its length the shore is protected by a steel

sheet pile sea wall. The remainder of the shore is sandy beach and a stone rubble jetty enclosing a small boat docking area.

Immediately northeast of the jetty is a dock which, until recently, served as a berth for two aircraft carriers. At the junction of the sea wall and beach is a storm drain outfall. This is the approximate center of the study area".

Figures 46 and 47 indicate the study area and physical features throughout.

All Bay testing was performed in September, 1974. The operations were conducted from the Ocean Engineering Research vessel Crows Nest VI.

After the boat was anchored at each data point, the microlaterolog was lowered and voltages of the bottom sediment and water immediately off the bottom were recorded. Due to the boat's natural movement at anchor, a series of formation factors at each data point actually covered a small area. The microlaterolog was then hauled to the surface and a sample was obtained using the Shipek Sediment Sampler, model 860, manufactured by Hydro Products. The samples were stored in air and watertight plastic bags until tests were conducted at the University of Rhode Island Soil Mechanics Laboratory.

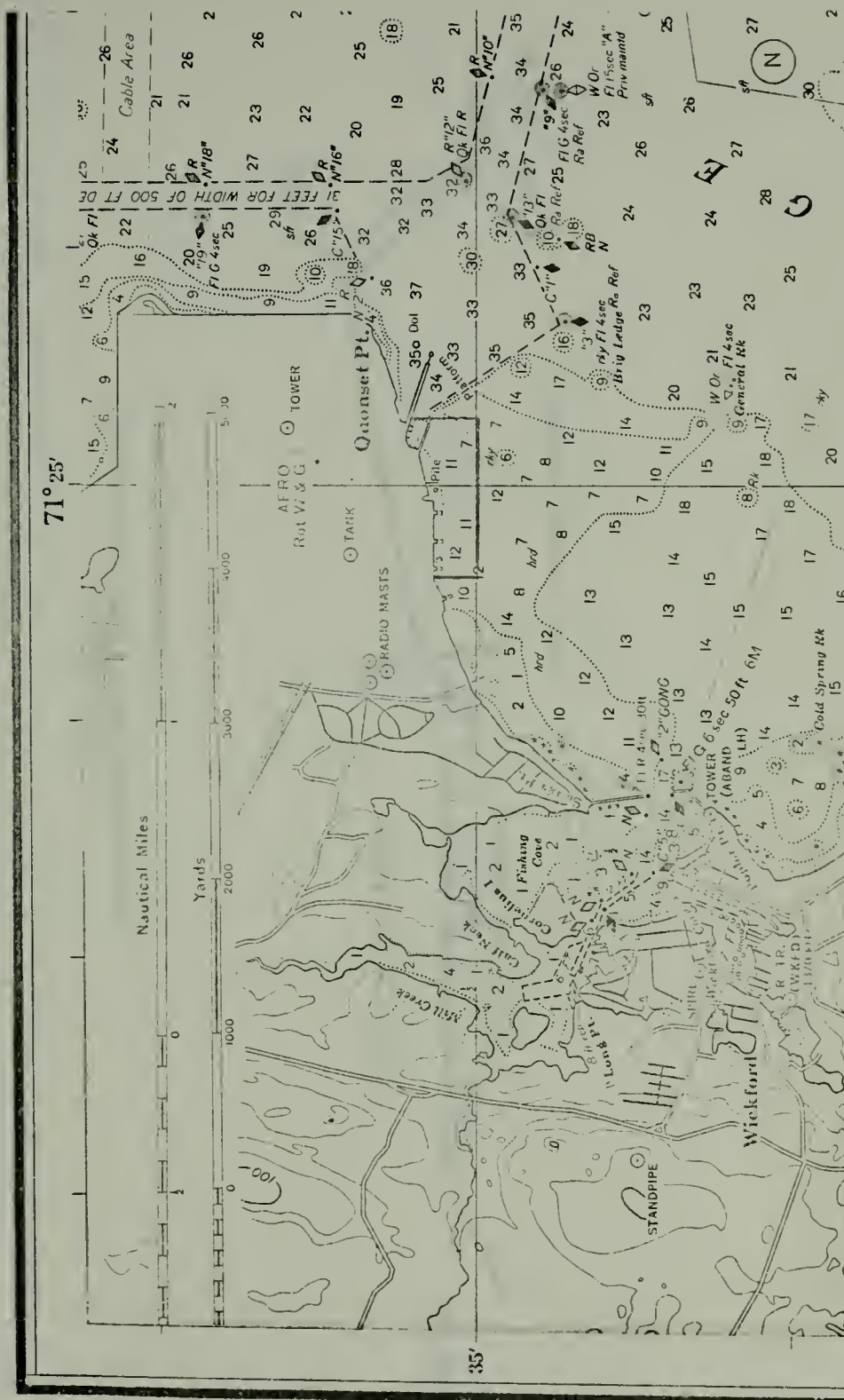


FIGURE 46. Study Area

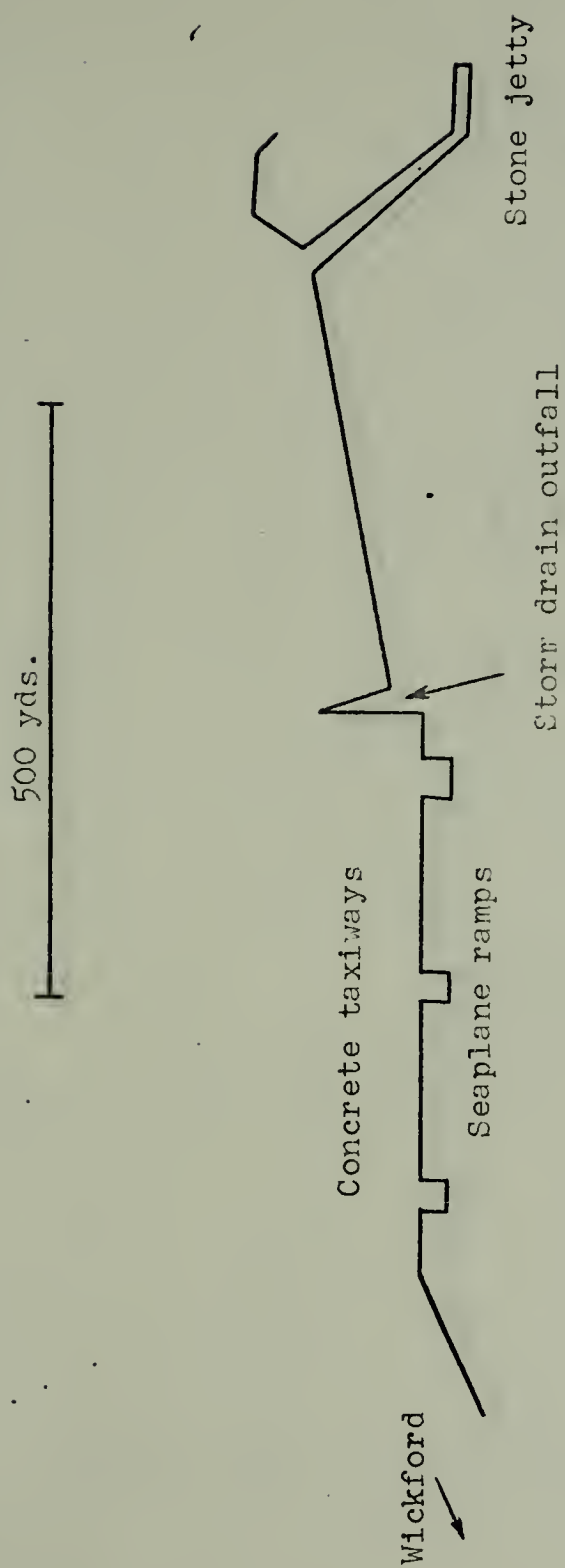


FIGURE 47. Study Area, Enlarged View

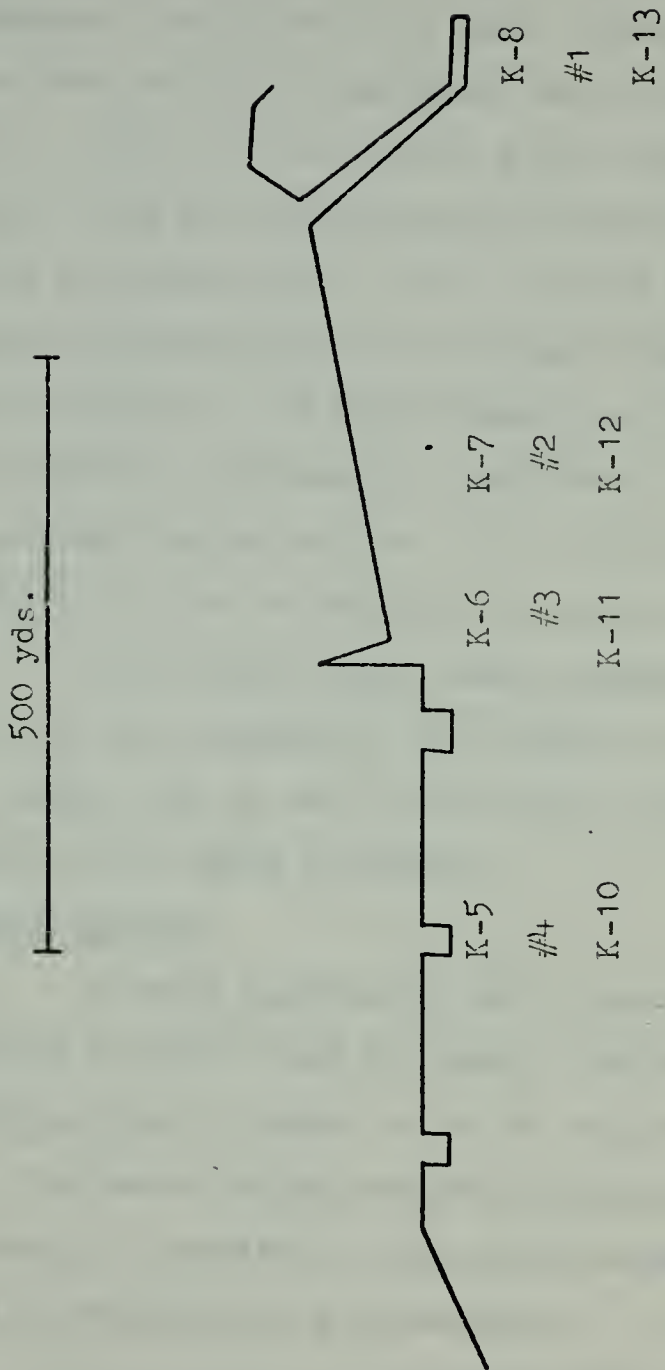


FIGURE 48. Sampling Points

This author felt that four sediment samples would provide a good correlation to Killoy's work. Figure 48 indicates the eight sites where Killoy took soil samples and the four sites where this author took soil samples. Three of this author's four sampling sites fell in areas where Killoy discovered extraordinary concentrations of pollutants (#2, 3, 4). It was felt that if any pollution concentrations had changed, these areas would be prime targets. The fourth sampling site (position #1) while certainly not devoid of pollution, had no such extraordinary concentrations. It, therefore, seemed a good choice to run an additional analysis.

Six primary tests were conducted on the soil samples in the laboratory. All tests were as indicated by either Lambe (26) or Baird and Killoy (24). A brief synopsis of the tests performed:

1. Water Content

A small quantity of soil (approximately 50g) was oven-dried at 105° C for 24 hours. The weight lost by this oven-drying is taken to be the weight of interstitial water. The water weight divided by the weight of the sample after drying is defined as the water content. The ratio is typically expressed as a percentage.

$$\text{Water content} = \frac{\text{Weight of water}}{\text{Weight of soil}} \times 100\% \quad (14)$$

2. Specific Gravity

Approximately 30 grams of oven-dried soil was crushed with a rubber-tipped pestle and run through the Beckman Air Comparison Pycnometer. Several informal analyses between the Beckman method and the standard bottle method for specific gravity determination conducted in the University of Rhode Island Soil Mechanics Laboratory have shown the value of the Air Comparison Pycnometer.

Knowing the water content and specific gravity of a submerged soil sample (granular saturation equal to 100%), it is quite easy to determine the void ratio, E , of the sediment by

$$\begin{aligned} ES &= WG \\ S &= \text{Saturation (100\%)} \\ E &= \text{Void ratio} \\ W &= \text{Water content} \\ G &= \text{Soil specific gravity} \end{aligned} \quad (15)$$

And void ratio and porosity are related through the equation

$$N = \frac{E}{1 + E} \quad (16)$$

Therefore, porosities of the samples can be easily calculated.

3. Grain Size Analysis

A large quantity of oven-dried soil (between one hundred and two hundred grams) was broken up using the mortar and rubber-tipped pestle. This sample was then sieved through a set of sieves (#40, 60, 80, 100, 200). As per Lambe (26), if more than 20% of the sample passed

through the #200 sieve, a hydrometer analysis was also performed. From the combined analyses, a percentage of sand (grains larger than 0.06 mm), silt (grains between 0.06 mm and 0.002 mm), and clay (grains less than 0.002 mm) was obtained. In addition, the uniformity coefficient for each sample was determined. This quantity, U , is a measure of how alike or uniform the soil particles are over the range. It is defined as the ratio of the particle size having 60% of the sample finer divided by the particle size having only 10% finer. A large uniformity coefficient (> 6) implies a well-graded soil, while a smaller (< 6) implies a uniform soil. Naturally, a uniformity coefficient of 1.00 would be indicative of a soil with all grains the same (such as a basket of marbles).

4. Organic Content

A small sample of dried soil was oxidized with 30% hydrogen peroxide. Fresh hydrogen peroxide was added until no reactions were observed. The soil was washed and filtered, then oven-dried. The weight lost through the oxidation procedure divided by the final dried weight is taken as the organic content, again expressed as a percentage.

5. Hydrocarbon Content

This quantity was determined by heating the soils from which organics had been removed (as above). It was

performed in a muffle furnace at 600° C for five hours. The weight lost by heating divided by the soil weight after heating is the hydrocarbon content. This term is typically presented as a percentage.

The above two oxidation processes in tandem provide an approximate value for volatile solids within the soils.

6. Heavy Metals Analysis

Five grams of oven-dried soil had organics destroyed through the addition of 40 ml of concentrated nitric acid and 20 ml of concentrated sulfuric acid. This solution was then heated until SO_3 fumes appeared. After cooling, 75 ml of distilled water and 0.10g of ammonium exalate crystals were added to remove any nitrogen oxides. The solution was again heated and this time evaporated until SO_3 fumes were evident. The solution was cooled and diluted to 200 ml total volume.

After filtering, the solutions were analyzed for heavy metals on the Perkin-Elmer Atomic Absorption Spectrograph. Results were obtained in parts per million of heavy metals in solution. Knowing the dilutions carried out throughout, the author then determined the pollutant concentrations in micrograms of pollutant per gram of soil.

Data and Results

Tables 8 and 9 are composite listings of the

results of the above soil and pollution tests run by this author on his four sampling points and by Killoy on the eight sampling points of his survey closest to those of this author. The Killoy points are prefaced by a "K".

Table 10 is a listing of formation factors for the four points from this survey combined with formation factors for the eight proximity Killoy points.

Interpretation

Prior to any analysis of pollution data, it is most important to verify that the Quonset Point soils investigated by this author have not changed substantially from those analyzed by Killoy. Obviously, a change in soil characteristics could yield a change in formation factors regardless of pollution levels.

In this regard, the two most important soil characteristics would be sediment classification and porosity. The important relationship between formation factor and porosity has been previously discussed. Equally important is the relative grain sizes within a sample. This soil size distribution has a direct effect upon the path that the electrical current must take. This is the tortuosity discussed in the first section of this paper:

$$T = [(FF)(N)]^{\frac{1}{2}} \quad (8)$$

Erchul (16) has shown that as the tortuosity increases

TABLE 8. Field Sediment Characteristics

<u>Sample</u>	<u>Water Content %</u>	<u>Specific Gravity</u>	<u>Porosity %</u>
1	30.31	2.65	44.53
K-8	24.49	2.66	39.45
K-13	29.59	2.67	44.13
2	68.30	2.64	64.32
K-7	52.54	2.67	58.56
K-12	44.37	2.67	54.22
3	47.99	2.63	55.79
K-6	32.58	2.66	46.40
K-11	37.27	2.72	50.34
4	96.55	2.61	71.59
K-5	68.08	2.61	63.99
K-10	72.70	2.69	62.86

TABLE 8. Field Sediment Characteristics (continued)

<u>Sample</u>	<u>Sediment Classification</u>			<u>Uniformity Coefficient U</u>
	<u>% Sand</u>	<u>% Silt</u>	<u>% Clay</u>	
1	100	-	-	1.67
K-8	88	12	-	3.86
K-13	49	50	1	2.50
2	50	49	1	3.52
K-7	50	43	7	14.17
K-12	67	28	5	7.85
3	68	31	1	2.67
K-6	28	68	4	3.61
K-11	51	44	5	7.27
4	54	46	-	6.43
K-5	83	17	-	11.54
K-10	32	56	7	15.75

TABLE 9. Pollutants in Field Samples

<u>Sample</u>	<u>Organic Content %</u>	<u>Hydro- Carbons %</u>	<u>Volatile Solids %</u>	<u>Heavy Metals*</u>		
				<u>Cr</u>	<u>Fe</u>	<u>Zn</u>
1	1.57	0.50	2.07	12	12,160	112
K-8	2.20	1.46	3.66	20	6,780	81
K-13	1.48	0.90	2.38	10	9,000	40
2	8.19	1.75	9.94	40	16,960	164
K-7	4.87	1.82	6.69	10	7,600	118
K-12	3.11	1.36	4.47	10	8,300	70
3	3.37	1.13	4.50	12	14,800	180
K-6	3.81	1.87	5.68	20	6,450	118
K-11	2.56	1.98	4.54	50	10,630	60
4	7.07	2.51	9.58	72	19,200	216
K-5	4.11	10.52	14.63	20	6,490	150
K-10	6.01	2.35	8.36	60	11,200	162

*

µg of pollutant per gram of soil

TABLE 10. Formation Factors in Study Area

<u>Sample</u>	<u>Formation Factors</u>
1	2.60 2.62 2.53
K-8	2.72
K-13	2.81 1.83
2	2.29 2.00 2.05
K-7	2.42 2.90
K-12	2.86
3	2.23 2.03 2.36
K-6	1.96 1.98 2.32
K-11	2.04 2.34 2.20
4	2.27 2.57 2.28
K-5	1.94
K-10	2.18 2.51 2.46

(due to a better graded soil), the conductivity of the sediment decreases and the formation factor increases. Armed with these two parameters, soils of the Quonset area may be compared.

From Table 8, sample #1 fits K-8 along both sediment classification and porosity just a little better than K-13. Sample #2 compares more favorably to K-7 than K-12. K-12 has a much more distributed sediment classification. Sample #3 fits K-11 along sediment classification considerably better than K-6. Finally, sample #4 appears to be somewhere between K-5 and K-10; however, a little closer to K-10. Two-year pollution comparisons can now be performed between #1 and K-8, #2 and K-7, #3 and K-11, and #4 and K-10.

Very little change was observed in organic content, hydrocarbon content and volatile solids. The values do help to confirm site locations and comparison points. Analysis of heavy metals yields much more interesting results. While chrome concentrations remained relatively constant, iron and zinc levels increased substantially. Sample #1 had 79% higher iron and 38% higher zinc concentrations than sample K-8. Sample #2 had 123% more iron and 39% more zinc than K-7. Sample #3 had 39% more iron and 200% more zinc than K-11. Finally, sample #4 was 71% higher in iron and 33% higher in zinc than K-10. From the

laboratory work done on zinc and iron, a predominantly granular sediment would be expected to increase in conductivity with the addition of those two metal ions. This, in turn, would cause a decrease in formation factors. A comparison of formation factors in Table 10 shows that just a situation was observed. Formation factors obtained in November, 1974 on soils that were more polluted with heavy metals were generally lower than formation factors read on the same soils in September, 1972.

It must be pointed out that all Quonset Point soils tested by this author had changed the uniformity and sediment classification since the Killoy report. Furthermore, the changes were towards more uniform soils which would decrease tortuosity and decrease formation factor. However, a close look at sample #2 shows that the pollutant level cannot be ignored. Here, the soil agreed most nearly with Killoy's samples. The sediment classification between #2 and K-7 is indeed almost exact. Nevertheless, a very substantial decrease in formation factors was observed, in the presence of very high pollutant levels. The micro-laterolog did detect the pollutant level changes!

VI. CONCLUSIONS

1. This study has demonstrated that an electrical conductivity device can detect common pollutants in marine sediments. Due to the common electrical effects of the tested pollutants, the tested device is recommended more for monitoring a known site rather than attempting to detect pollution in previously uncharted soils.

2. Particular value for the conductivity pollution monitor is seen for industries desiring to monitor discharge for a particular chemical. Once the electrical effects of the desired pollutant were plotted, the microlaterolog could easily monitor discharge points for presence of the pollutant.

3. The device demonstrated its ability to detect an increase in pollutants in actual marine sediments over a two-year time frame. Such an ability precludes extensive coring to monitor ocean sediment pollution. The easier microlaterolog readings can be taken, and as long as no substantial changes in formation factors are observed, coring can be avoided. Conversely, if formation factor changes are apparent, cores can be taken in selected areas.

4. Conductivity readings are so easy and inexpensive to obtain that extended ocean bottom analysis is possible.

VII. RECOMMENDATIONS FOR FURTHER STUDY

The author has but one rather sweeping recommendation for further study. It stems from a feeling that little research coordination is evident among graduate students.

Pollution is, of course, the subject for research today. Environmental concern has modified old practices and even stopped new construction. Yet research on the actual quality of life is in the state-of-the-art technology.

One proposal for marine study would be the establishment of an ocean microcosm. The most obvious form would be a marine aquarium, complete with natural marine sediments and sealife. Joint efforts could be provided by graduate students with interests in biology, civil engineering (particularly sanitary and environmental), and ocean engineering.

Various pollutants would be added to the microcosm and the effects on all ocean phases monitored. Here, the microlaterolog device would be valuable in observing the sediments. Once desired pollution levels were reached within the microcosm (sediments, plants, animals, water), unpolluted sea water could be added. It seems probable that information obtained could lead to suitable prediction techniques regarding the quality of life in the ocean,

also the self-cleansing ability of the ocean and all its phases.

This type research would seem to be extremely useful in assessing the impact man has had on the oceans by past actions and also his predicted impact in the future.

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APPENDIX

Manufacturer's Instrumentation Information

CONDUCTIVITY SIGNAL CONDITIONER DESCRIPTION

INTRODUCTION

The Conductivity signal conditioner is a solid state null balance a-c amplifier. It supplies the current to drive the conductivity sensor, and compares the resultant output of the sensors with a stable reference voltage. A differential voltage is used to regulate the drive current and produce an output linearly proportional to the conductivity of the measured solution. Output signals can be in the range of 0-5, 1-5, or 0-10 V dc. A 0-50 mv output is also provided for functional checks and calibration.

All signal conditioners are physically standardized for interchangeable mounting and wiring in signal conditioner modules, 19" relay-rack adaptor housing, or single unit panel-mounted cases. They are available in high density, non-indicating, 1/8-rack width modules (eight to a 5 1/4" x 19" relay rack) or indicating, 1/4-rack width modules (four to a 5 1/4" x 19" relay rack). Any combination of 1/8 and 1/4-rack width modules can be assembled within the limitations of a 5 1/4" x 19" relay rack adaptor housing. Indicating (1/4-rack width) modules have taut-band suspension panel meters ($\pm 1/2\%$ FS) with separate span adjustments, customized scale markings, and a scale mirror to eliminate parallax errors.

All primary operating controls are front-of-panel mounted. Included is a 3-position, calibration check switch used for instant verification of the operating precision of the signal conditioner, independent of the sensor. Pilot lamps are optionally available for use as front-panel visual indicators of power failure. Two other versions are not illustrated at right; one has no range switch, and the other has no range switch but has automatic range change indicator lights.

MODULAR CONSTRUCTION

Both indicating and non-indicating models share a common design and use identical, interchangeable components. A quick-connect type main chassis with retractable mounting track and extension cable allows front withdrawal with access to all operator adjustments and test points while signal conditioner is in extended position and energized.

All main chassis contain a printed wiring "motherboard" that accepts separate, plug-in, measuring, amplifying, and power supply printed wiring boards built with edge-connect plugs for card-file guiding during circuit insertion and withdrawal. All card tongues are arranged to mechanically ensure correct board placement without component damage from inadvertent interchanges.

RANGE CONVERSION

All conductivity signal conditioners have $\pm 20\%$ span and zero adjustments for field recalibration when replacing sensors. Range changes beyond these adjustability limits are readily accomplished by changing a plug-in card containing fixed range resistors.

Output ranges are convertible from 0-5, to 1-5, to 0-10 vdc for use with commercial analog and digital recorders or standard telemetering equipment. See ordering data for available ranges.

151 0015 552

CONDUCTIVITY SIGNAL CONDITIONER DESCRIPTION

TEMPERATURE COMPENSATION

Since solution conductivity varies with operating temperature, compensation is required to refer the measurement to standard conditions (usually 25°C). Models are available for use with either fixed or adjustable temperature compensation. In both forms a thermistor is built into the sensing unit. With fixed compensation, the output of the thermistor directly alters sensor current to maintain a fixed output vs. input relationship independent of solution temperature. Compensation is factory-set to follow the KCl curve (approximately 1.84% per °C). With adjustable compensation, the thermistor is connected to an adjustable compensation network in the conditioner which alters the reference voltage to match sensor output vs. input voltage change with solution temperature. The range of adjustment from approximately 1.4 to 2.5% per °C allows compensation to be adjusted for other than the KCl curve and permits tracking solution temperature changes within closer tolerances.

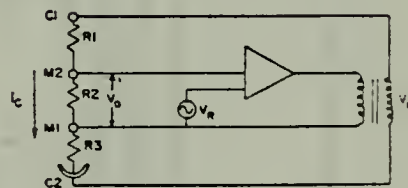
POWER SUPPLY AND ISOLATION

Conductivity sensors must be operated from an a-c power source to prevent polarization. In addition, the solution being measured is usually at some ground potential which differs from the parametric system output or power line grounds. For these reasons the conductivity signal conditioner, which powers the sensors, includes a power supply both internally synchronized and isolated from ground and input is isolated from output. All a-c voltages and modulation circuits are synchronized to the a-c power source at 50 or 60 Hz. The power transformer has separate conductivity - isolated secondary windings connected to full-wave rectifiers and appropriate zener diode regulation circuits to provide separate floating d-c signal and output power supplies. All a-c voltages are generated by solid state chopping of appropriate d-c voltages at the power source frequency.

OPERATING PRINCIPLE

The conductivity signal conditioner operates on potentiometric principles. A self-balancing a-c circuit is used with either of four interchangeable conductivity sensors. An a-c current I_c is applied through two sensor current electrodes, C1 and C2. The resulting voltage drop V_0 across two measuring electrodes, M1 and M2 is compared with fixed a-c reference voltage V_r . When they differ, the resulting error voltage V_c alters sensor drive current I_c . The amplifier system then changes its output to maintain V_0 equal to V_r . Since V_0 is held constant, drive current I_c is by ohm's law, inversely proportional to solution resistance and therefore directly proportional to its reciprocal, conductivity.

Although not shown, the actual circuit includes provisions for signal isolation, d-c voltage output, and measurement with the high parametric system accuracy (\pm FS) required by this application.



151-0015-552

552-0-1



7730 AC-45

7:50 AM - 8:00 AM

YSI PRECISION THERMISTOR

Model #44001

RESISTANCE 100 OHMS AT 25°C

TIME CONSTANT¹ . . . 1² sec. max., 10³ sec. max.

DISSIPATION

CONSTANT¹ 6² mw/°C., 1³ mw/°C.

COATING CODE . . . Black epoxy on body of thermistor with brown end

1. MINIMUM OPERATING TEMPERATURE and other side of this sheet

2. Heat sinks (needle nose pliers, etc.) when soldering or welding to thermistor leads.

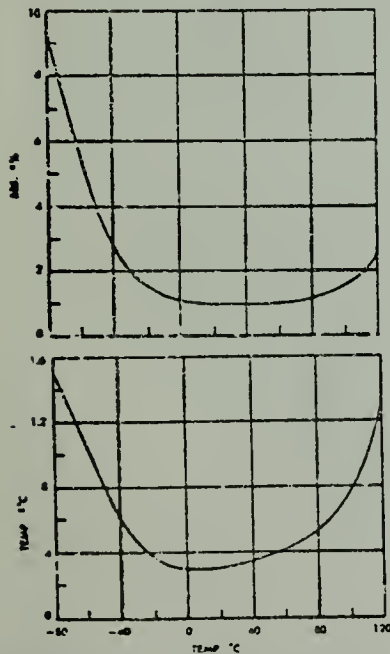
3. Time constant is the time required for the thermistor to indicate 65% of a new impressed temperature.

4. Values determined with thermistor suspended by its leads in a "well stirred" oil bath.

5. Values determined with thermistor suspended by its leads in still air.

6. The dissipation constant is the amount of power in milliwatts required to raise the thermistor 1°C above the surrounding temperature.

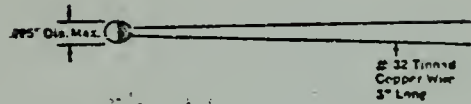
TOLERANCES



YSI COMPONENTS DIVISION

P.O. BOX 579,
YELLOW SPRINGS, OHIO 45387

YSI PRECISION THERMISTOR



RESISTANCE VERSUS TEMPERATURE -80° to +120°	
TEMP °C	RES. OHMS
-80	282
-70	285
-60	288
-50	291
-40	294
-30	297
-20	300
-10	303
0	306
10	309
20	312
25	315
30	318
40	321
50	324
60	327
70	330
80	333
90	336
100	339
110	342
120	345

MAXIMUM OPERATING TEMPERATURES

Maximum operating temperature 150°C. Long term stability studies show that extended operation of this piece above 90°C or continued cycling to temperatures above 90°C will cause a resistance increase which will exceed thermistor tolerance. When these operating conditions are expected YSI suggests use of YSI Precision Thermistors with values at 25°C of 2252 ohms or higher. These higher resistance value pieces have not shown such shifts in our studies.

Thesis
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In-situ detection and
monitoring of marine
sediment pollution
through electrical con-
ductivity methods.

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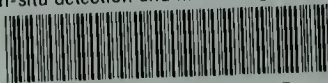
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